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EPARATION OF TRACES OF INORGANIC IONS FROM AQUEOUS SOLUTIONS BY
GAS-, LIQUID- AND SOLID-PHASE DISTRIBUTION PROCEDURES

(Review)

T. S. WEST, *Anal. Chim. Acta*, 25 (1961) 405–421

HE EFFECT OF HEAT ON SOLUTIONS OF CERIUM(IV) SULPHATE IN SULPHURIC
ACID AND SOME ANALYTICAL IMPLICATIONS

eric sulphate solutions may undergo appreciable losses of cerium(IV) on heating. The overall loss
acid dependent, being at a minimum in about 1 M sulphuric acid, and is almost independent
the cerium(IV) concentration. Consequently as the concentration falls the actual percentage
ss increases. The loss, resulting from the reaction of cerium(IV) with water, is catalysed hetero-
neously at the glass surface and also on the surface of any precipitated material. The extent of the
ss varies considerably with the conditions of the experiment. Solutions of ceric sulphate prepared
om commercial grade cerium(IV) sulphate or ceria and from spectroscopically pure ceria, behave
the same fashion. The effect of added silver(I), copper(II), mercury(II) and phosphite ions in
e cerium(IV)–water reaction is reported.

D. GRANT AND D. S. PAYNE, *Anal. Chim. Acta*, 25 (1961) 422–428

EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

II. DETERMINATION OF COPPER, NICKEL, IRON, CHROMIUM AND VANADIUM

method for the determination of nickel, copper, iron, chromium and vanadium by the addition
excess EDTA and back-titration with standard cobalt solution is recommended. The titration
volves an extractive method of end-point detection, depending on the appearance of the blue
lour of the ion-association pair [Ph₃MeAs]₂[Co(SCN)₄] in chloroform. The method is therefore
itable for the determination of these metals in highly coloured aqueous solutions. The maximum
pected error is of the order of 1 %, and in the majority of determinations the error is 0.5 % or less.

A. J. CAMERON AND N. A. GIBSON, *Anal. Chim. Acta*, 25 (1961) 429–433

XIDIMETRIC DETERMINATION OF URIC ACID WITH POTASSIUM IODATE OR PERIODATE

(in French)

acid is determined by potentiometric titration with potassium iodate or periodate in solutions aining hydrochloric acid. Depending on the acid concentration the reagent is reduced to e monochloride, or to elementary iodine (in the case of iodate).

APPLICATION OF SELENIUM SALTS IN INORGANIC ANALYSIS

gravimetric determination of metals as selenides is proposed. Owing to the rapid atmospheric ation of sodium selenide and the toxic nature of hydrogen selenide, special apparatus is ired. The methods are analogous to precipitation of sulphides. Arsenic, tin, antimony, plati-, ruthenium, palladium, rhodium, rhenium, mercury, silver and gold can be determined. thermolysis of precipitates formed with arsenic, antimony, mercury, silver, rhenium, plati-, ruthenium, palladium and rhodium has been studied.

MINATION OF DISTILLATION IN THE KJELDAHL METHOD FOR THE MICRO- SEMIMICRO-DETERMINATION OF NITROGEN IN NITRO, NITROSO AND AZO COMPOUNDS

ethod is described for the determination of nitrogen in nitro, nitroso and azo compounds by eldahl method without distillation. The compound is reduced with glucose or zinc in methanol hydrochloric acid. The ammonium sulphate produced after the usual digestion is determined ypochlorite–arsenite titration. A single vessel is used for reduction, digestion and titration.

CATION-EXCHANGE BEHAVIOR OF CALCIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

cation-exchange behavior of calcium on Dowex 50W-X8 is described. Nitric acid, hydrochloric , ammonium chloride, sodium nitrate, ammonium acetate and citric acid are examined as nts. Calcium can be separated from copper(II), zinc(II), cadmium(II), mercury(II), iron(III) from barium. Separation factors for barium–calcium and barium–strontium are evaluated.

A CONTINUOUS FLOW MONITOR FOR SCANNING ^{32}P-CONTAINING EFFLUENTS FROM CHROMATOGRAPHY COLUMNS

ontinuous flow monitor for scanning ^{32}P-containing effluents from chromatography columns escribed. The separation of ^{32}P-labeled compounds from barley is presented as an illustration e results obtained with the system.

ETECTION OF CARBAMATE-FORMING METALS IN PRESENCE OF ALUMINIUM
AND OTHER METALS BY RING OVEN AND SPOT COLORIMETRY. I.

(in German)

nall amounts of cations yielding insoluble dithiocarbamates are fixed on filter paper by precipi-
tion with Na-DDTC. Other cations are removed by washing. On the Weisz-Ring oven, the metal-
DTC is moved to the ring by washing with pyridine *without* prior drying. Identification is carried
t in the ring zone, if necessary after destruction of carbamate and removal of interfering cations.
.—Al is given as example.

H. MALISSA AND L. J. OTTENDORFER, *Anal. Chim. Acta*, 25 (1961) 461–462

PECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM
WITH SOLOCHROMATE FAST RED

method is described for the spectrophotometric determination of micro amounts of uranyl ions
th the azo dye, Solochromate Fast Red, which reacts with uranium(VI) in acetate-buffered
ethanol solution to form an orange-brown colored complex with maximum extinction at 490 mμ.
er's law is obeyed over a wide range of uranium concentrations. Only a limited number of foreign
ns interfere, hence this method is generally applicable after removal of interfering ions by anion
change; *e.g.* uranium can be determined in marine materials.

J. KORKISCH AND G. E. JANAUER, *Anal. Chim. Acta*, 25 (1961) 463–469

SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM
WITH STANNOUS IODIDE REAGENT

idium ions react with tin(II) iodide reagent to form a stable complex with an absorption maxi-
um at 446 mμ. Beer's law is not obeyed but the reaction is reproducible and the absorbancy is
oportional to iridium concentration with an accuracy of $\pm 0.9\%$ over the range 0.8–11.7 p.p.m.
ior separation of iridium from rhodium and other transition metals is necessary. The procedure
mpares favorably with the tin(II) bromide method. The tin(II) halide reactions with platinum
oup metals are shown to diverge from true homologous series.

E. W. BERG AND H. L. YOUMANS, *Anal. Chim. Acta*, 25 (1961) 470–475

SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH
1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID

balt(III) forms a water-soluble complex with complexone IV. The violet complex has an ab-
rbance maximum at 545 mμ and obeys Beer's law from 1 to 100 μg cobalt per ml. The complex
easily prepared and a procedure for the spectrophotometric determination of cobalt in acid
edium is given. In this method only large amounts of chromium cause significant interference.
e complex contains the cobalt and the reagent in a ratio of 1 : 1, the molar extinction coefficient
305 and the stability constant of the complex is $8.5 \cdot 10^{21}$.

E. JACOBSEN AND A. R. SELMER-OLSEN, *Anal. Chim. Acta*, 25 (1961) 476–481

VOLTAMMETRY AT INERT ELECTRODES

I. CORRELATION OF EXPERIMENTAL RESULTS WITH THEORY FOR VOLTAGE AND CONTROLLED POTEN-
TIAL SCANNING, CONTROLLED POTENTIAL ELECTROLYSIS, AND CHRONOPOTENTIOMETRIC TECHNIQUES.
OXIDATION OF FERROCYANIDE AND o-DIANISIDINE AT BORON CARBIDE ELECTRODES

An exhaustive study of linear diffusion techniques has been carried out at B_4C electrodes. In addition to proving the utility of B_4C electrodes for both practical and theoretical investigations, some novel inter-relationships between modern electrochemical techniques have been developed, and the validity of the RANDLES–SEVCIK equation has been established for slow scan rates.

SEPARATION BY VOLATILIZATION OF THE RADIOISOTOPES OF PLATINUM, IRIDIUM, OSMIUM AND RHENIUM FORMED BY BOMBARDMENT OF A GOLD TARGET

(in French)

The radioactive isotopes of mercury, platinum, iridium, osmium and rhenium — products of bombardment processes in gold irradiated with prótons at 150 MeV — are separated cleanly by distillation in a stream of argon or chlorine and by condensation in a tube possessing a temperature gradient.

NOTE ON THE VERY SENSIBLE DETECTION OF PERMANENT GASES BY GAS CHROMATOGRAPHY BY MEANS OF A METASTABLE HELIUM DETECTOR

(Short Communication; in French)

THE REACTIONS OF DIPHENYLCARBAZIDE AND DIPHENYLCARBAZONE WITH CATIONS

(Short Communication)

eview

EPARATION OF TRACES OF INORGANIC IONS FROM AQUEOUS OLUTIONS BY GAS-, LIQUID- AND SOLID-PHASE DISTRIBUTION PROCEDURES*

T. S. WEST

Chemistry Department, University of Birmingham (Great Britain)

(Received April 4th, 1961)

he determination of trace amounts of inorganic constituents in solutions of commer-
al materials and particularly in the analysis of pure metals for atomic plants, semi-
nductor materials for the electrical industry, etc. is a key problem in modern
alytical chemistry. In the majority of instances, satisfactory chemical or instru-
ental methods are available for the determination of microgram or even submicro-
am amounts of ions provided that they can be supplied to the reaction vessel or
strument in a suitable chemical form. Usually this means that as far as possible,
ey should be presented in a relatively pure solution free from the bulk constituent
d with the minimum amount of indifferent electrolyte. Consequently it is desirable
separate or concentrate the minor constituents away from the bulk material by
phase separation process, *i.e.*

Sample → Bulk constituent + trace
[Phase I]   [Phase II]
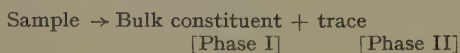
addition it is generally desirable that the trace should be removed into the second
ase leaving the bulk constituent behind in the original medium, since this is usually
sounder proposition experimentally and it permits the operation of a concentration
age. There are of course many exceptions to such a generalisation. For example,
the determination of impurities in silica in many cases the bulk constituent may
removed as volatile silicon fluoride by treatment with hydrofluoric acid. Similarly
determining traces of other substances in tin salts advantage may be taken of the
latility of stannic iodide to remove the tin and leave the traces behind; and yet
ain, in the analysis of elements such as sulphur in steel[1] ferric chloride may readily
extracted into amyl acetate leaving the sulphur as sulphate in virtually pure
lution ready for rapid complexometric determination.

However, these are exceptional examples of removal of a bulk constituent and
bsequently throughout this paper only the removal of the trace constituent is
nsidered. Separation by the newer techniques of ion-exchange or chromatography
any of its many forms is precluded from this discussion, which is therefore con-
rned with what might be termed the classical separation methods, *viz.* removal
the trace in a second phase, which can therefore only be gas, liquid or solid.

Before considering these three methods in order, it should be stated here that the following discussion is in no way intended to be exhaustive. The relevant information is scattered widely throughout the literature and the present choice mainly reflects the interests of the author. It should also be stressed at this point that little systematic work has been done on the evaluation of separation methods on a comparative basis. Many conflicting claims exist and whilst these have been avoided largely in the following paragraphs, this has not always been possible. In several instances also it has not been made clear in the original papers what the upper and lower limits of separation are. This is not entirely surprising when it is remembered that the separation procedures merely appear as a means towards an end in most analytical papers. On the whole, however, most of the following procedures are valid for μg (10^{-6} g) amounts and a considerable number also for millimicrogram (10^{-9} g) or smaller amounts. Such small quantities are of course physically invisible to the unaided human eye.

GAS PHASE SEPARATIONS

It is well known that most of the non-metals can be separated from aqueous solutions as volatile products. For example, boron may be removed as steam-volatile boric acid or as methyl borate, carbon as carbon dioxide, nitrogen as ammonia or various oxides, sulphur as hydrogen sulphide, etc. This requires little further comment. For minute amounts it is advantageous to use a carrier gas from which the trace can be isolated by chemical or physical absorption or by differential freezing. It is less generally appreciated, however, that several metals and metalloids can also be isolated by distilla-

TABLE I

ELEMENTS CONCENTRATED BY DISTILLATION FROM HCl–HBr ($t = 220°$)*

1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac**															
			Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th**	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No			

* Non-metals enclosed within black-line may be distilled in a variety of ways.

n or evolution from an aqueous phase. This presents a fairly selective separation of
se few metals from most others, but even within the group a certain degree of selec-
ity of separation can be achieved by physical and chemical control of the medium.
ble I summarises the volatilisation of chlorides and bromides[2] from a medium con-
ning three other common mineral acids, *viz.* perchloric, sulphuric and phosphoric, in
 temperature range 200–220°. Chromium distils quantitatively from perchloric acid
ner as bromide or chloride. Ruthenium and osmium behave in exactly the same
y and none of the three appears to distil at 220° either as chloride or bromide from
ulphuric acid medium. On the other hand antimony distils quantitatively as bro-
de from either sulphuric or perchloric acid. Phosphoric acid, however, will hold
ck the normally volatile chloride. Tin and germanium behave in a fashion more or
s identical to antimony.

Valency control is also an effective means of increasing the selectivity in many
es. In the last example for instance, 100% recovery of arsenic(III) chloride can
obtained from sulphuric acid, but only 5% of arsenic(V). Both valence forms yield
antitative recovery as bromides. Within this same framework, the separation of
 closely similar elements may perhaps be mentioned.

Osmium–ruthenium. A medium of 5 *M* nitric acid treated first of all with hydrogen
oxide or ferrous sulphate yields only osmium tetroxide on distillation. Subsequent
noval of any chloride ion and evaporation with a sulphuric–perchloric acid medium
l cause quantitative distillation of μg amounts of ruthenium.

Arsenic–antimony[3,4]. At a temperature $\leqslant 107°$ only arsenic(III) chloride will distil.
e antimony will distil subsequently on raising the temperature. Hydrazine is
ommended to maintain the valence of the arsenic throughout the process. Germa-
m, if present, accompanies the arsenic(III).

These few examples alone are chosen to typify this method of separation. Generally
 alternative procedure would be attempted because on the whole the chemical
kground and manipulative technique of distillation is more difficult than that of
 other techniques which follow. However, the use of organic reagents has scarcely
 entered this branch of separation chemistry, though the volatilisation of methyl
ate is a well known example. It is recognized that several metal chelates *e.g.* the
tylacetonates of several metals may be distilled without decomposition and the
atility of certain 8-hydroxyquinoline metal-ion compounds is a source of difficulty
many analytical experiments. The entry of organic reagents into this region may
l revolutionise our approach to the use of this rather selective separation technique.

SOLVENT EXTRACTION

he second phase which is to be separated off from the aqueous solution is itself a
iid phase then we are most certainly concerned with the preferential partition of
 inorganic trace-ion across a liquid–liquid phase boundary into a water-immiscible
anic solvent. The phenomenon of precipitation of a non-miscible liquid phase from
aqueous solution of inorganic ions is practically unknown.

 cation in aqueous solution exists largely as an aquo-ion complex with all possible
 coordination positions occupied by water molecules. This and any secondary
regation of water molecules results in a water-jacketed ion which, whether we
sider things fundamentally on the basis of Hildebrand's theory of regular solutions[5]

in terms of solubility parameters, etc., or on the simple rule-of-thumb dictum that 'like dissolves like', tells us that such ions have little chance of punching a hole in the liquid–liquid interface to pass through and mix smoothly with the organic molecules which almost certainly will have a much lower dielectric constant.

In order to make the ion pass the phase boundary it is necessary to divest it of all or most of its water molecules and replace them by other firmly coordinated groups which, when bound to the ion, possess the minimum of ionic character. The groups (ligands) will coordinate in a stepwise fashion if unidentate in character or if multidentate will coordinate in a smaller number of steps according to the requirements of the ion. In the latter case the entropy effect of the replacement of two or more water molecules by only one of reagent and the inherent strength of subsequent ring closure is likely to result in circumstances more favourable for successful extraction.

It can readily be shown, after making certain simplifying assumptions concerning the equilibria involved, that the ratio of the total of metal-ion species in the organic phase to the total of metal-ion species in the aqueous phase can be related very conveniently to the fundamental parameters of the system by the expression

$$D = \frac{K_C K_{CD} K_R{}^n}{K_{RD}{}^n} \cdot \frac{[HR]_0{}^n}{[H^+]_{Aq}^n}$$

i.e.

$$D = k' \cdot [HR]_0^n / [H^+]_{Aq}^n$$

where D is the distribution ratio, K_C is the instability constant of the extracting species MR_n, K_{CD} is the partition coefficient of the extraction species, K_R is the acid dissociation constant of the protonated form of the ligand *i.e.* HR, K_{RD} is the partition coefficient of the ligand R^-, $[HR]_0$ is the concentration of the protonated ligand in the organic phase, $[H^+]$ is the concentration of hydrogen ion in the aqueous solution and n represents the number of R^- groups coordinated to each metal ion (M).

Splitting this expression into two parts as shown, it is apparent from that in choosing a reagent the stability constant (k') should be as high as possible, the partition coefficient of the complex as high as possible and the acid strength of the protonated ligand also as high as possible (*i.e.* R^- should have a low affinity for H^+), and finally the distribution coefficient of the free ligand should be as low as possible. The last mentioned two factors are particularly important since they may operate through the exponent $n \geqslant 1$.

Taking the second half of the expression into account it is apparent that once the reagent has been selected, the acidity of the aqueous phase $[H^+]_{Aq}$ should be minimal and the concentration of the acid species of the reagent in the organic phase as high as possible.

If two metals extract simultaneously then the separation which may be expected between them is defined by the separation factor β: $\beta = D_1/D_2$ where D_1 and D_2 are the appropriate distribution ratios, $D = \Sigma[M]_{org}/\Sigma[M]_{Aq}$.

The law of electrical neutrality is a good peg on which to hang any chemical calculation. In the instance of extraction, it clearly indicates that whereas a cation may readily pass a phase boundary if it is locked up in an undissociated neutral molecule, it cannot pass in the ionic form (cationic or anionic) unless it takes with it an equal

charge concentration of the opposite polarity, *i.e.* it must pass in association with other counter ions.

This type of system is known as an ion-association system. Neutral molecules may usually be classified within the chelate extraction system since most organic reagents contain both ionogenic and coordinating groups in such a way that the principal valence and coordinate requirements of the ion are simultaneously satisfied by the reagent. This results in a neutral molecule with no attached water groups.

Ion-association systems

The extraction of most inorganic ion-association systems is found to depend markedly on the nature of the extracting solvent. This is so because most of these systems still have the ion bound to some remaining coordinated water molecules (similarly with the counter-ion) and usually it is the case that it is possible for these to be replaced by molecules of oxygen-containing organic solvents such as ethers, ketones, esters, alcohols, etc. Once these solvent molecules are bound to the extracting ions it is not difficult to understand why the latter may then pass the phase boundary to intermingle smoothly with the solvent molecules. The similarity of molecular structure also explains why most ion-association systems extract well at high concentration. The selective nature of the solvent can be explained on several grounds, but one of the chief factors appears to be stereochemical. In practice this appears to be more important than the basicity of the oxygen atoms. Thus on the grounds of basicity one would predict an order of efficiency of alcohols > ethers > ketones, but the steric factor introduced by the more accessible promontory position of a carbonyl as opposed to a chain-linked oxygen results in ketones being generally preferable to ethers.

It is also found that the addition of fairly large amounts of electrolyte frequently aids the extraction. These added electrolytes can of course act through a common-ion action, but frequently this is not the most important factor. The binding up of a large proportion of the available water molecules in the aqueous solution within the coordination spheres of the ions of the salting-out agent appears to be a much more decisive item and also the considerable lessening of the dielectric constant of the aqueous solution. This last factor greatly favours ion-pairing, etc.

Chloride ion systems. The chloride ion system was used in 1892 by ROTHE[6] for the ether extraction of ferric chloride from a strong hydrochloric acid system. Many elements extract well from hydrochloric acid into a variety of oxygen-containing organic solvents, *e.g.* Sc, Fe, Ga, Ge, As, Nb, Mo, Sb, Pt, Au, Tl, Po, Pa, all *ca.* 100% with large amounts of Hg, V, Sn, Te and small amounts (*ca.* 1%) of Co, Ni, In, and Ir, whilst others such as Cu, Zn, Mn, Cr, Zr, Ag, Pb, Cd, Bi are unaffected.

Within the group of extractable ions, selectivity can be introduced by chemical control of the medium. Thus the lower oxidation states of iron, thallium and antimony do not extract appreciably whilst upon oxidation it is found they all extract efficiently. The reverse is true for elements such as tin, and arsenic. Then again, at low acidity the extraction of iron(III) is negligible, but gold(III) and mercury(II) extract well. When the acidity is raised mercury(II) no longer extracts, but iron(III) does whilst gold still extracts. The influence of solvent choice may be cited for the cobalt/nickel system. If the acidity is controlled at 4.5 M a separation factor $\beta_{Co/Ni}$ of 70 can be achieved with *n*-octanol[7].

Bromide ion systems tend to be more selective in nature. The group 3b elements

Ga, In, Tl all extract well, as do Fe, Au, Hg and, to a lesser extent (>50%), As, Sb, Sn. Moderate extraction (ca. 30%) occurs with Se, Mo and small amounts (ca. 1%) of Cu, Zn, Pd, Te and Pt also partition. Again chemical control enhances selectivity. Thus Fe, Cu and Tl are favoured in the oxidised state, but scarcely extract following reduction. The situation is reversed for Pt. Acidity control is also effective as before.

Iodide ion systems. The behaviour of iodide ion systems is summarised in Table II. In this case it is noticeable that lead and cadmium now extract well. Some authors find iron to extract[8] whilst others do not[9]. With this system it is convenient to work with an acidified solution of potassium iodide instead of with free hydriodic acid.

TABLE II

ELEMENTS EXTRACTED FROM IODIDE ION-ASSOCIATION SYSTEMS

1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

Key for Tables I and II

- complete extraction
- good extraction (>50%)
- ca. 30% extraction
- ca. 1% extraction

Fluoride ion systems. Fluoride ion association systems present the most selective separations within the halide group. Only Nb, Ta, Pa extract efficiently though some authorities found quantitative extraction of tin(II) and (IV)[10] and others disagree[11]. Further selectivity is also possible within the group, however, for a β-value of 880 is obtained[12] for the Nb/Ta system in 0.4 M hydrofluoric acid. Only tantalum extracts well at this acidity.
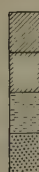
Thiocyanate ion systems. Lastly the pseudo-halide thiocyanate ion system is con-

sidered since it is a suitable connecting link with chelate systems. Most ion association systems function best at very low pH when masking agents cannot usually be applied to increase selectivity. Thiocyanate and most chelate systems function better in the normal pH range (0–14) where masking and pH control are on the whole, much more effective. Table III shows the situation with thiocyanate. The system is not as un-

TABLE III

ELEMENTS EXTRACTED FROM THIOCYANATE ION-ASSOCIATION SYSTEMS

1.	H																He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	**Ac															
			*Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			**Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

Key

▨	complete extraction
☐	good extraction (>50%)
▤	ca. 30% extraction
▦	ca. 1% extraction

selective as appears at first sight, for remarkable changes can be brought about by masking and pH control, etc. Even two such unpromising systems as rare earths–thorium[13] and zirconium–hafnium[14,15] (extraction of the first named metals) can be resolved in this instance.

Chelate systems. Most of the organic reagents used in inorganic analysis for the precipitation of weighing forms may be used for extraction since the metal ions are usually fully coordinated by the reagent, surrounded by a bulky envelope of organic molecules, screened from solvent effects, etc. The nature of the solvent is much less critical with such systems and even unpromising materials such as benzene, kerosene, carbon tetrachloride, etc, may be used. With few exceptions, however, the solubility

of most metal chelates in organic solvents is not very high and in contrast to ion association systems they are not suitable for bulk extractions. On the other hand, the effects due to ring formation, entropy differences, etc. all tend to make the sensitivity of such systems rather high.

Oxine. 8-Hydroxyquinoline is well known for its ability to precipitate some 30 cations in normal gravimetric work. Most of these chelate compounds are extractable into solvents such as chloroform under specified pH conditions, *cf.* Table. IV. Used in

TABLE IV

OXINE EXTRACTION SYSTEMS

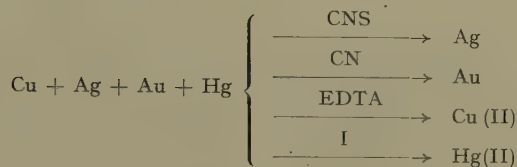|																		
1.	H																	He
2.	Li	Be												B	C	N	O	F	Ne
3.	Na	Mg												Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

high concentration at high pH, even the alkaline earths will extract, thus demonstrating the validity of the $[HR]_o/[H^+]_{Aq}$ factor in the equation previously mentioned. At the pH where most of these extractions occur masking action may readily be applied. For example, cyanide ion addition prevents extraction of the strong complex formers such as iron, copper, nickel, molybdenum[16,17], but leaves others such as lead and manganese susceptible to removal. EDTA has a similar role to play with Al, Co, Mn, Fe, Ni whilst acetate ion[18] may mask thorium and iodide masks mercury(II).

MERRITT AND WALKER's reagent[19], 8-hydroxyquinaldine, with its sterically hindering 2-methyl group is inactive towards aluminium so that a double extraction first with this reagent and subsequently with oxine[20] provides a clean separation of aluminium from practically all other metals. Further modification of the reagent can yield higher selectivity along other directions. Thus as an example, the use of 5,7-dichloro-8-hydroxyquinoline by MOELLER AND JACKSON[21] may be quoted.

The strong fluorescence of oxine chelates is useful for determining small traces of metals, following extraction, directly in the organic phase without further processing. Concentrations at the 0.1-p.p.b. region can readily be extracted.

Dithizone. Dithizone extracts well in the middle ranges of the periodic table and since its potentialities are well known by virtue of the use of its tinctorial powers in absorptiometric analysis, little mention need be made of it here. It can also be rendered highly selective by masking action. Thus in presence of excess of EDTA and thiocyanate only mercury(II) is extracted by dithizone; in the presence of cyanide and thiocyanate only mercury(II) and copper(II), and in presence of EDTA (alone), mercury (II) and silver[22].

Selective phase stripping is sometimes useful for increasing selectivity. Thus if a dithizone extract contains Hg + Cu + Au + Ag shaking up of the layer in turn with the named reagent in aqueous solution causes back-extraction of the ions as follows:

$$Cu + Ag + Au + Hg \begin{cases} \xrightarrow{\text{CNS}} & Ag \\ \xrightarrow{\text{CN}} & Au \\ \xrightarrow{\text{EDTA}} & Cu\,(II) \\ \xrightarrow{\text{I}} & Hg(II) \end{cases}$$

Cupferron is another excellent all-purpose extraction agent[23], whilst many other more selective extractants may be used. For example dimethylglyoxime extracts only palladium(II) in $1\,M$ sulphuric acid[24], whilst only iron(II) and nickel partition from a basic pyridine medium[25]. High specificity may also be obtained by the phenanthroline and 4,7-diphenyl-1,10-phenanthroline systems (iron(II) and copper)[26] but in this instance the system involved depends on both chelation and ion-association.

Acetylacetone

One further chelate system should be mentioned. This is dependent on $\beta\beta'$-diketones such as acetylacetone. Acetylacetone has been investigated extensively by FREISER and his coworkers[27]. The reagent, being virtually a water immiscible liquid, may be used as its own solvent. Consequently because of the similarity of structure between the metal–chelate and the solvent molecules, high solubility and extraction power is possible so that acetylacetone may be applied equally well to macro and micro amounts. The following metals may be extracted: Be, Ti, V, Cr, Mn, Fe, Cu. In the presence of EDTA only beryllium and uranium(VI) are extracted and on a kinetic basis chromium(III), a slow reactor, may be separated from iron(III), copper(II) and molybdenum(VI). Cobalt and nickel are not normally extracted but cobalt(III) is readily partitioned, so a separation is easily obtained between the two.

Extraction of anions

Finally, mention should be made briefly of the extraction of anions as well as of cations. Only one example can be quoted here, namely the work of SMITH AND PAGE[28] on the use of N-methyl-di-*n*-octylamine in chloroform as an extractant for mineral acids from solution (*cf.* Table V).

This procedure presents a neat method of removing unwanted acidity without either increasing the ionic strength of the medium — as in neutralisation with alkali, or increasing the volume markedly — as for example in ion-exchange. Metals which exist in the anionic form can readily be extracted, *e.g.* vanadium(V) and chromium

(VI), and a separation is possible between niobium and tantalum (cf. Table VI)
based on the selective extraction of the chloride complex of niobium by this same

TABLE V

EXTRACTION OF ACIDS INTO 5% METHYLDIOCTYLAMINE IN CHLOROFORM

Acid	N	Equivalent of amine used	% In aqueous layer	% Recovered
Acetic	0.1	2.0	3	90
Chromic	0.1	1.5	2	97
Hydrochloric	1.0	1.0	1	98
Nitric	0.1	1.2	0	98
Oxalic	0.1	1.2	4	98
Phosphoric	0.21	1.2	44	50
Succinic	0.37	1.0	11	90
Sulphuric	1.0	2.0	1	98
p-Toluene sulphonic	0.05	1.2	3	97

TABLE VI

EXTRACTION OF NIOBIUM AND TANTALUM BY 5% METHYLDIOCTYLAMINE IN XYLENE FROM AQUEOUS
HYDROCHLORIC ACID

HCl M	% Extraction	
	Nb	Ta
2	4.0	—
2.9	—	0.25
3	2.4	—
4	2.2	—
4.85	—	0.11
6	21.5	—
7.28	—	0.55
8	99.3	—
8.85	—	1.10
9.6	100	—
10.10	—	1.35
11.2	—	1.40

reagent system. Much recent work has been done along these lines and in this respect
the work of F. L. MOORE and his coworkers, published mainly in *Anal. Chem.* is
noteworthy.

Extensive reviews of solvent extraction methods are readily available[29,30].

SOLID PHASE SEPARATION

It is often argued that precipitation is far inferior to solvent extraction as a separation
process for trace amounts and this is true because all precipitates have a finite solu-
bility and precipitation is a unit process as opposed to extraction which is dependent
solely on a distribution *ratio* and may therefore be operated as a repeated batch-pro-
cess or continuously. However, *direct* precipitation is not the analogue of extraction
and therefore this argument against precipitation is misleading. The precipitation
analogue of solvent extraction is what might be termed a solid–phase distribution

technique in which the trace ion existing in solution is caused to migrate preferentially across a phase boundary into a pre-existing or newly forming *solid* phase. This technique which may more loosely be called coprecipitation is just as sensitive as solvent extraction, as will be seen from the following paragraphs.

Solid–phase distribution proceeds by virtue of several processes including: (*a*) mixed crystal formation (isomorphism) in which the extracted ion penetrates into the host crystal and mixes intimately with its molecules; (*b*) solid solution, since most crystals are possessed of some degree of mutual solubility; (*c*) chemical compound formation; (*d*) adsorption, which is largely a surface phenomenon controlled by crystal lattice forces and the nature of the liquid medium in contact with the surface; (*e*) occlusion, *i.e.* mechanical trapping or entrainment by the host-precipitate particularly when it is freshly formed *in situ*.

Before considering these various factors further it is well to state clearly that the use of host precipitates (gathering agents) allows traces of ions to be deposited from solution at concentration levels where the ion-product of the trace salt nowhere near exceeds its solubility product. Thus the technique allows separation to be achieved well below the limiting barrier of normal solubility.

A homogeneous distribution law for mixed crystal formation may readily be defined by the expression $D = K_{mx}/K_{tx}$, where K_{mx} and K_{tx} represent the solubility products of the host precipitate and the trace salt respectively. Obviously, for large distribution ratios the host precipitate should be considerably more soluble than the trace precipitate, but it should still be sufficiently insoluble to allow the ratio $[M^{+n}]_{Precipitated}/[M^{+n}]_{Solution}$ to be *ca.* 100. It is quite common, however, for homogeneous distribution not to be present during precipitation or even after considerable ageing. In this case the distribution in the surface layers must be considered. According to DOERNER AND HOSKINS[31] the relationship may then be expressed logarithmically as:

$$\frac{\log [t]_{Total}}{[t]_{Solution}} = \lambda \frac{\log [M]_{Total}}{[M]_{Solution}}$$

where λ represents the logarithmic distribution coefficient governing heterogeneous distribution of tX throughout MX. In practice it is usually found that the behaviour of the system is intermediate between the two conditions represented by these equations.

Usually it is better to form the solid phase in the medium rather than to add it as a solid because advantage may then be taken of most of the factors involved and of course larger and more reactive surface areas may be obtained with nucleating precipitates. Furthermore, it is frequently advantageous to reverse the conditions normally obtaining in gravimetric analysis so that the precipitates are formed with maximal nucleation. The solid phase formed may be allowed, in most cases, to undergo particle growth by the process of self-induced recrystallisation caused by the relatively high solubility of the small particles.

Choice of collector

The influence of the various distributing mechanisms previously mentioned on the choice of the host precipitate may be discussed very briefly. Generally *mixed crystal formation* is advantageous when it may be applied, because it tends to promote selectivity and high distribution ratios. The host precipitate should be chosen to be

more soluble than the trace compound and the ionic radii of M and t should lie within $\pm$ 10% of each other. Again, the choice of *compound formation* as the gathering mechanism is likely to result in group selectivity, *e.g.* the use of tellurium to collect gold — probably as telluride — results in simultaneous collection of the other noble metals. When surface adsorption is the mechanism, the PANETH–FAJANS–HAHN rule[32] indicates that if the host precipitate is brought down with an excess of M^{+n} ions and is more soluble than tX then exchange of M and t ions will tend to occur at the surface, even though the solubility product of tX has not been exceeded. In the case of *mechanical trapping*, a voluminous precipitate is obviously advantageous. If the host crystals are soft (low surface tension) then ageing will at least not be harmful, but if they are hard and of high surface tension then the ratio of the solubility of the small primary particles of precipitate to those of the massive crystal (S_r/S) will be high as shown in the equation[33],

$$\frac{RT}{M}\,^e\!\log\frac{S_r}{S} = \frac{2\sigma}{dr}$$

where S_r denotes the solubility of a small particle of radius r; S the solubility of massive crystals of precipitate, σ the surface tension, d the density and M the molecular weight, so that ageing will promote considerable crystal growth and liberation of occluded trace material. S_r/S for barium sulphate crystals of radius 0.02 is *ca.* 600 whilst for calcium sulphate it is only *ca.* 3.

The subsequent treatment of the trace may also of course determine the choice of the host precipitate. In this respect, volatile compounds such as those of Hg, As, Sb, Sn may be most useful. The host phase may be filtered or centrifuged off in the usual way, but if the amount is small it may be advantageous to form the collecting

TABLE VII

CATIONS CONCENTRATED BY ZnO ADDITION

|																		
1.	H																	He
2.	Li	Be										B	C	N	O	F	Ne
3.	Na	Mg										Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac**															
			Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th**	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

precipitate in the interstitial spaces of a filter paper. Thus for example cadmium sulphide may be used in this way to collect traces of copper in nickel or lead salts when these are dissolved up and the copper is only at the p.p.b. level[34].

The collection of traces by this technique has been reviewed recently by SANDELL[35]

TABLE VIII

CATIONS CONCENTRATED ON SULPHIDES OF Hg, Cu, Pb AND Cd

1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac**															
			Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th**	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No			

Key

Cu
Hg
Pb
Cd

and elsewhere by the author[36]. Both these reviews approach matters from the viewpoint of the metal being concentrated. In the rest of this paper some (by no means all) of this information is collated from the viewpoint of the collector being used. It is presented largely in tabular form for ease of consultation, but this may obscure the measure of selectivity that is frequently possible by control of the experimental conditions.

Zinc oxide. Zinc oxide is mentioned first since it is more often than not added in the solid state to the solution containing the trace ion. Its use is thus more closely related to solvent extraction than that of most other collectors which are normally formed freshly by direct precipitation in the medium containing the trace. As a recent example of its use, mention may be made of the work of REYNOLDS AND SHALGOSKY[37] on the determination of traces of indium in cadmium in the 1–10 p.p.m. range.

TABLE IX COLLECTION OF VARIOUS IONS ON THE HYDROXIDES OF (a) ALUMINIUM, (b) IRON(III) AND (c) MANGANESE(IV)

(a)

1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

(b)

1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

(c)

1.	H																	He
2.	Li	Be											B	C	N	O	F	Ne
3.	Na	Mg											Al	Si	P	S	Cl	A
4.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5.	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6.	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7.	Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No		

TABLE X

CATIONS CONCENTRATED ON COPPER OXINATE

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**															
		Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th**	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No			

Cu on Pb oxinate; Ca with oxine only.

TABLE XI

CATIONS CONCENTRATED BY METHYL VIOLET—IODIDE SYSTEM

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**															
		Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th**	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Mv	No			

n as CNS; W as tannin/methyl violet; Ce/Eu as hydroxy-sulphophenylazodiphenyl derivative

Sulphide collectors

Many sulphides may be used to collect traces of other metals which form insoluble sulphides. The use of cadmium sulphide to collect copper from nickel and lead salts has already been mentioned[34] and it also has been used to gather iron and mercury. Some remarkable examples of high gathering power have been reported for this series as witness the collection of 0.02 μg of mercury from 1 l of solution on copper(II) sulphide[38] and of 1 μg of gold from 1000 l of sea water on lead sulphide[39].

Hydrous oxides of aluminium, iron(III) and manganese(IV)

These are all very efficient gathering agents though their selectivity may appear to be somewhat low at first sight. A few typical examples of their use are cited below to illustrate their sensitivity and range of application.

Aluminium hydroxide has been used for the concentration of 1 μg of titanium[40] from 1 l of solution.

Iron(III) hydroxide has been applied to the concentration of 0.1 μg of vanadium from 1 l of solution[41] and for the separation of μg amounts of palladium from mg amounts of silver[42].

Manganese(IV) oxide may be somewhat more selective than the others. Thus it has been applied to the separation of antimony and thallium in copper and lead salts[43] and also for tin from arsenic and copper[44].

Organic reagents

Many organic reagents have been used such as mandelic acid[45,46], anthranilic acid[47], cupferron[48] and 8-hydroxyquinoline[49]. The behaviour of copper oxinate as a collector is shown in Table X[50].

Lastly, special mention should be made of recent Russian work on methyl violet–iodide as a collecting agent. Metals gathered by this system are shown in Table XI. High selectivity can be obtained for certain metals within the group. Indium for example can be recovered at a dilution level of 1 μg in 20 l selectively in the presence of all the other ions which coprecipitate with this system[51]. This is done by limiting the amount of iodide added when all the other metals coprecipitate without the indium. Subsequently the addition of more iodide and methyl violet to the filtrate brings down the indium. A 20–30-min standing time is required and a 0.5 M sulphuric acid medium is used.

Copper can also be coprecipitated selectively within the group[52]. This is done by coprecipitating from a medium containing free iodine. Copper is masked by this procedure and may then be brought down by reducing the iodine in the filtrate through addition of hydroxylamine.

In conclusion it is hoped that these few examples of the concentration of traces of inorganic ions from aqueous solution by the technique of solid phase distribution will serve to focus some attention on its potentialities as an analytical tool. It is probable that systematic examination of the technique, particularly in relation to solvent extraction, may prove that it is at least equally effective and complementary.

University Symposium on Analytical Chemistry for the opportunity to present this paper and also wishes to acknowledge his indebtedness to the publications of SAN-DELL[35] and of MORRISON AND FREISER[29] as valuable sources of information.

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THE EFFECT OF HEAT ON SOLUTIONS OF CERIUM(IV) SULPHATE
IN SULPHURIC ACID AND SOME ANALYTICAL IMPLICATIONS

DAVID GRANT AND DOUGLAS S. PAYNE

Department of Chemistry, The University, Glasgow (Great Britain)

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INTRODUCTION

It is commonly stated[1] that cerium(IV) sulphate solutions are stable when heated. This distinctive feature of cerium(IV) sulphate solutions has resulted in their application in numerous analytical methods involving the use of an excess of reagent at, or near, the boiling point, the residual oxidising agent subsequently being determined by titration with a suitable reagent.

The use of cerium(IV) solutions in analytical chemistry has been reviewed recently by YOUNG[2] and PETZOLD[3]. PETZOLD has summarised the literature on the stability of cerium(IV) solutions and quotes the figures of WILLARD and YOUNG[4]. According to the details given in their 1929 paper, these workers found that samples of 0.1 N cerium(IV) sulphate in 0.9 to 1.8 M sulphuric acid showed no losses after boiling under reflux for up to 5 h. It is not commonly recognised that in a later paper (1930) WILLARD AND YOUNG, in reporting the reaction of various organic acids with cerium-(IV) sulphate in sulphuric acid solution under analytical conditions, mention the need for corrections of "0.03–0.05 ml" to allow for the loss of oxidising agent on boiling. The occurrence of this "blank" in these experiments was attributed to the oxidation being carried out in a beaker, whereas in the previous experiments, in which no blank was detected, a flask and reflux condenser were employed. In the experiments described, involving relatively unreactive organic acids such as formic or acetic acids, losses of cerium(IV) amounting to up to "0.21 ml" were encountered. BERRY[5], who in 1929 investigated the use of boiling cerium(IV) solutions for the quantitative oxidation of tartrates, reported that he had repeated WILLARD AND YOUNG's first set of experiments and confirmed the stability of cerium(IV) sulphate. Solutions of cerium(IV) containing appreciable concentrations of nitrate or perchlorate ions were early shown to lack analytical stability on boiling[4]. SMITH AND SULLIVAN[6] have observed only slight changes ($\pm 0.03\%$) in an approximately 0.1 N solution of ceric ammonium nitrate in sulphuric acid, of concentration up to 0.5 M, after heating at 100° under a reflux condenser for periods of time as long as 3 h.

In marked contrast to these observations, WEISS AND SIEGER[7] have reported significant losses, of 13 to 20% in 0.1 N cerium(IV) sulphate solutions on boiling, the loss being minimised by the addition of silver sulphate. Their experimental details are, however, meagre and it is difficult to appreciate fully the significance of their results. PETZOLD[3] has commented that these results might well have arisen from the presence

traces of material which could act catalytically in reactions involving the loss of
erium(IV) from solution, such as

$$2 \, Ce^{+4} + H_2O \rightarrow 2 \, Ce^{+3} + 2 \, H^+ + \tfrac{1}{2}O_2$$

his latter reaction is thermodynamically possible in acid solution, as is shown by
he high value of the redox potential of Ce(IV)/Ce(III) in sulphuric acid ($E_0 = 1.44$ V
$25°$ in $1 \, M$ sulphuric acid), compared with that for the oxidation of water in acid
olution, ($2 \, H_2O \rightleftharpoons O_2 + 4 \, H^+ + 4 \, e$; $E_0 = -1.229$ V at $25°$)[8]. The values for the redox
otentials of the Ce(IV)/Ce(III) couples in nitric and perchloric acid are higher still,
hese solutions being appreciably less stable than the sulphuric acid system.

Although it is customary to refer to cerium(IV) solutions in terms of Ce^{+4}, this ion
known not to be present in appreciable amounts, if at all, when ligand groups such
sulphate or nitrate are present; however, there are in these solutions which are
ly stable in the presence of acid, appreciable amounts of anionic species containing
erium(IV). Only in perchloric acid solution is the Ce^{+4} ion probably present to any
reat extent. The crystal structure of certain basic salts obtained from solution shows[9]
em to contain poly cations such as $[Ce_6O_4(OH)_4]^{+12}$. Species of this kind containing
veral cerium(IV) atoms may be present in the cerium(IV) solutions as employed.
hatever the true nature of the species present, it is to be expected, in general,
at the behaviour will be dependent on the acid concentration. Solutions with pH
alues up to 4 are of particular interest since this range is readily accessible; in the
se of solutions of pH approaching 4 a situation of incipient precipitation arises.

In commenting upon the stability of cerium(IV) sulphate solutions, it is relevant
note that ceric oxide reacts with concentrated sulphuric acid on heating with
ppreciable reduction of the cerium(IV), and that from time to time various ill-defined
asic salts containing both cerium(IV) and cerium(III) have been reported to be
otained from sulphuric acid solution of cerium(IV) compounds, often merely on
anding; further investigation of these observations is clearly desirable.

METHODS

ur attention was drawn to the inherent instability of acid ceric sulphate solutions
temperatures above $40°$ by difficulties encountered in the analysis of certain
osphites by the method of BERNHART[10] in which for the oxidation, an excess of
ric sulphate is used at the boiling point. RAO AND RAO[11] have drawn attention to
e inconsistency of the results by this method and have proposed the use of silver(I)
n as catalyst, thus enabling the reactions to be carried out at slightly lower temper-
ures and with a shorter heating time.

Investigation showed that acidified ceric sulphate solutions underwent loss of
idation equivalent on heating and that this loss was dependent upon a number of
ctors. The reaction taking place is reduction of cerium(IV) with resultant oxidation
water, as is shown by the restoration of the cerium(IV) by treatment with sodium
smuthate of the cerium(III) produced. The extent of the loss varied considerably,
general being below about 2% for approximately 0.1 N cerium(IV) sulphate solu-
ns in 1.5 M sulphuric acid, heated for up to 1 h under reflux; values as high as 20%
ay, however, be encountered for approximately 0.01 N cerium(IV) sulphate solu-
ns. At temperatures below reflux the extent of the reaction is considerably less,

being in general below 1%. It is intended to publish an account of these and other experiments later, but it seems of importance at this stage to report such aspects of the work as are relevant to the analytical application of cerium(IV) sulphate solutions.

EXPERIMENTAL

Experiments were conducted by heating various volumes of cerium(IV) sulphate solutions for varying times under specified conditions and observing the decrease in ferrous ammonium sulphate titre. Solutions were, as far as possible, always titrated under the same conditions, ferroin being employed as indicator. It was established that loss of cerium(IV) occurred even at temperatures as low as 45° and that an appreciable difference in behaviour exists between solutions in which boiling actually occurred, and those in which it did not.

There is a distinction between solutions below and those at the reflux temperature as regards the extent of the loss quoted earlier, and also the dependence of this extent on the physical conditions of heating. In both, the loss of cerium(IV) occurs in the course of an initial zero order reaction which comes to an abrupt stop after various periods of time up to 30 min. The rate of this initial reaction is much greater at the boiling point than at lower temperatures. The length of time for which it occurs and hence the extent, depends on physical factors, there being a dependence on the solution–glass surface area ratio and type of heating at reflux temperature. At lower temperatures the reaction time depends on the reaction rate, which is probably controlled by the precise surface conditions, faster reactions proceeding for shorter times. The same inverse dependence is found for all temperatures (45–85°) studied below boiling point. As heating is continued, no further loss occurs until, for periods of heating longer than 1 h, some precipitation begins, catalysing further decomposition of the cerium(IV).

Below reflux temperature the rate of the initial reaction is probably dependent on the conditions of the surface of the vessel, the highest rate being achieved on treatment of the surface with boiling 3 M sulphuric acid for 25 min before use. Evidence suggests that repeated use of the vessels without this treatment leads to the extent of the loss becoming less. The deactivation of the surface of the vessel, probably by the products of the initial reaction, may lead to a situation where virtually no loss of cerium(IV) occurs on heating. This phenomena might well serve to explain the absence of loss found by other workers. As the vessel walls become catalytically inactive no visible deposit is apparent, although in certain experiments a white solid is sometimes seen. The variation in reaction rate with surface conditions results in wide variations in the extent of the reaction found after heating for a standard time, similar to that accepted as generally useful in quantitative cerium(IV) sulphate oxidations. For example, for a cerium(IV) solution of normality 0.145 N and sulphuric acid concentration of 1.5 M, after 30 min at 64° the loss varied from 0.03% to 0.3% depending on the pretreatment of the flasks. Variations in acid concentration led to an increase in the loss as the sulphuric acid concentration increased, optimum low values for the loss being at about 1 M. Below 0.5 M precipitation begins on raising the temperature, the precise acid concentration depending on the cerium(IV) concentration, and decreasing with decreasing cerium(IV) concentration. With this precipitation losses of cerium(IV) increase owing to the catalytic effect of the precipitate. It is possible to redissolve this precipitate by adding sulphuric acid before titration

Under certain conditions the precipitated material redissolves simply on cooling, although this is in general a slow process. Data on the variation of loss with acid concentration is shown in Table I.

TABLE I

20-ml portions of 0.145 N cerium(IV). Time of heating, 65 min. Temperature 87.0° ± 0.1°

Overall acid concentration	% loss
10	1.70
4.5	0.60
2.6	0.56
1.1	0.40
0.9	0.50
0.7	0.80

The effect of temperature is not a simple one, although one can state that below 40° the loss is in general negligible. Variation of loss with ceric solution normality below reflux temperature was not studied.

Experiments at the boiling point were carried out under reflux conditions, the temperature varying mainly with the acid concentration of the solutions studied. As the sulphuric acid concentration increases up to 5 M, the temperature gradually increases to 110°; with higher acid concentrations, considerably higher temperatures are attained, cerium(IV) solutions in 50% sulphuric acid refluxing at about 145°.

It became apparent that conditions of boiling (i.e. type of heating, extent of bubbling, even the shape of vessel) affected the results very markedly as is shown in Table II, in which variations with vigour of boiling are noted. The terms gentle, moderate and vigorous reflux refer to the rate of formation of bubbles.

TABLE II

VARIATION OF LOSS WITH CONDITIONS OF REFLUX

10 ml of a 0.0113 N cerium(IV) solution, overall acid concentration 1.3 M

	% loss
10 min under vigorous reflux	2.7
10 min under moderate reflux	1.6
73 min under vigorous reflux	7.9
73 min under moderate reflux	5.8
73 min under gentle reflux	2.5

The extent of the loss of cerium(IV) varies widely from experiment to experiment unless care is taken carefully to standardise the conditions, such as the agitation of the solution and the extent of interface between solution, flask and air. The effect of variation in cerium(IV) and acid concentrations, as well as volume of solution is shown in Table III.

If the acid concentration and the experimental conditions are constant the absolute loss of cerium(IV) equivalents tends to be independent of the cerium(IV) concentration. Consequently larger percentage losses are found for more dilute solutions. This

follows from the idea that the controlling factor is the catalytic activity of the glass surface which will be independent of the cerium(IV) concentration. The extent of the reaction can be increased by increasing the surface area of glass available, for

TABLE III

LOSS OF CERIUM(IV) IN PYREX GLASS VESSEL

Cerium(IV) concentration, N	H_2SO_4 concentration, M	Volume of solution ml	% loss Cerium(IV) during initial reaction
0.1191	2.4	25	1.34
0.0475	2.7	25	2.52
0.0835	1.5	10	4.19
0.0305	2.6	35	2.26
0.0762	2.6	35	0.68
0.0153	2.6	35	3.18
0.0414	2.2	35	1.24
0.0494	1.4	25	1.05

TABLE IV

VARIATION OF LOSS WITH ACID CONCENTRATION

(a) Samples of 20 ml 0.0056 N cerium(IV) sulphate heated under reflux for 40 min

(b) Samples of 50 ml 0.050 N cerium(IV) sulphate heated under reflux for 56 min

Concentration of H_2SO_4 M	% loss		Concentration of H_2SO_4 M	% loss
0.13	10.76		0.8	2.01
0.58	7.91		1.5	1.41
1.0	7.74		2.6	1.77
2.8	7.94		4.4	1.89
4.6	8.42		6.2	2.57
9.1	13.53		9.8	4.58

example by adding Pyrex glass helices. The effect of acid concentration is shown in Table IV.

PETZOLD[3] suggested that the erratic results of WEISS AND SIEGER[7] were due to catalysis of the cerium(IV)–water reaction by impurities. We have examined this point by using a solution of ceric sulphate prepared from spectroscopically pure cerium(IV) oxide and AnalaR reagent sulphuric acid, and we can find no difference in behaviour, as far as loss of oxidation equivalent on heating is concerned, between this solution and solutions prepared from commercial ceria or commercial ceric sulphate and commercial sulphuric acid.

The effect of added silver(I), copper(II), and mercury(II) ions on the loss of cerium-(IV) varies with the concentration of the ions; in general the extent of the loss on heating is increased. A decrease in the extent is, however, found for copper(II) when the concentration of copper(II) present is less than $4 \cdot 10^{-3}$ M. Larger concentrations increase the loss again. A careful study of reactions involving phosphite shows that here, although the loss is not eliminated, it may be substantially reduced.

The loss of oxidation equivalent in cerium(IV) solution is of obvious importance in analytical reactions which require a temperature much above room temperature. For reactions at reflux temperature the method of heating is important in view of the variability of the loss with the nature of the bubbling, etc. With this in mind the wide variations found by WEISS AND SIEGER[7] can be largely attributed to their method of heating, apparently on sand baths. RAO AND RAO[11] found it necessary to employ a boiling water bath in order to control the errors encountered in the oxidation of the phosphite by cerium(IV).

Two points emerge from this work. Firstly, the loss of oxidation equivalent varies widely depending very much on the conditions of the reaction. Secondly, it is not possible to evaluate in advance the effect of the various factors and consequently, when the reagent is employed in analytical reactions, care must be taken to investigate the magnitude of the blank carefully.

The evidence so far collected is indicative of a reaction between the cerium(IV) species and the water leading to the formation of hydroxyl radicals, which subsequently break down probably to gaseous oxygen. The reaction is apparently surface cata-

TABLE V

THE CERIMETRIC ANALYSIS OF PHOSPHITE[10] BY OXIDATION OF $SrH_2(HPO_3)_2$

(Theoretical equivalent weight 62.3)

Volume of a solution containing 1.859 g $SrH_2(HPO_3)_2/100$ ml	ml 0.1191 Cerium(IV) reacted	Apparent equivalent weight
0.2	0.94	33.4
0.5	1.64	47.9
1.0	2.82	55.7
2.0	5.19	60.5
5.0	12.57	62.4
10.0	24.25	64.7

Each solution had an initial cerium(IV) conc. of 0.0487 N, H_2SO_4 conc. 2 M and Ag(I) conc. (cf. ref.[11]) $6.1 \cdot 10^{-3}$ M.

On extrapolation of a plot of the ml cerium(IV) solution reacted against the amount of phosphite present to zero phosphite, a ''blank'' loss of cerium(IV) of 0.47 ml solution is found. This may be used to work out a corrected equivalent weight, a value of 64 being obtained from the gradient of the plot. If the equivalent weight (apparent) is plotted against the quantity of phosphite taken a plateau value is found near the theoretical equivalent at 62.3.

lysed and diffusion to the surface of the glass and the nature of this surface are clearly important factors in determining the rate of the reaction, although there is little evidence to suggest that the extent of the initial fast reaction is related in a simple fashion to the catalytic activity of the surface. The effect of the metal ions is to catalyse homogeneously the reaction of cerium(IV) and water, and thus increase the loss. Phosphite on the other hand will minimise the loss by reacting with the hydroxyl radicals almost as soon as they are formed at the surface of the vessel, thereby reducing the probability of the radicals reacting to give oxygen. We have found that phosphite complexes with cerium(IV) in sulphuric acid solution and that the oxidation of phosphite in these solutions, on heating, proceeds probably by way of reaction of phosphite ions with hydroxyl radicals. The incipiently formed radicals will thus be liable to interact with phosphite rather than to escape to the solution.

In the analysis of phosphites it has been found necessary to adopt a procedure whereby the oxidation equivalent is determined for different amounts of phosphite using a constant amount of ceric sulphate solution in sulphuric acid and the resulting data is then plotted to enable the loss of cerium(IV) to be evaluated (Table V). The appearance of solid material in the solution may make the loss considerably larger and the accurate assessment of the correction difficult.

CONCLUSION

It must be admitted that the work described above, whilst revealing the possibilities of serious errors in determinations based on the use of ceric sulphate solutions, does not offer any single solution to the problem, which must be treated and solved independently in every situation. Previous difficulties reported in certain applications of cerium(IV) sulphate solutions by other workers, now can be recognised as arising from the losses described above.

ACKNOWLEDGEMENT

SUMMARY

Ceric sulphate solutions may undergo appreciable losses of cerium(IV) on heating. The overall loss is acid dependent, being at a minimum in about 1 M sulphuric acid, and is almost independent of the cerium(IV) concentration. Consequently as the concentration falls the actual percentage loss increases. The loss, resulting from the reaction of cerium(IV) with water, is catalysed heterogeneously at the glass surface and also on the surface of any precipitated material. The extent of the loss varies considerably with the conditions of the experiment. Solutions of ceric sulphate prepared from commercial grade cerium(IV) sulphate or ceria and from spectroscopically pure ceria, behave in the same fashion. The effect of added silver(I), copper(II), mercury(II) and phosphite ions in the cerium(IV)–water reaction is reported.

RÉSUMÉ

Les auteurs ont effectué une étude démontrant que les pertes en cérium(IV), par chauffage de solutions de sulfate de cérium, dépendent principalement de la teneur en acide. La perte est minimum dans l'acide sulfurique 1 M et ne dépend pratiquement pas de la concentration en cérium(IV).

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass der Verlust an Ce(IV) beim Erhitzen einer Ce(IV)-sulfatlösung vom Säuregehalt der Lösung abhängt. Der Verlust ist am geringsten in einer 1 M Schwefelsäurelösung und ist unabhängig von der Ce-Konzentration.

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EDTA TITRATIONS WITH EXTRACTIVE END-POINTS

II. DETERMINATION OF COPPER, NICKEL, IRON, CHROMIUM AND VANADIUM

A. J. CAMERON AND N. A. GIBSON

Chemistry School, Sydney University, Sydney, N.S.W. (Australia)

INTRODUCTION

An extractive method of end-point detection has been applied to the titrimetric determination of cobalt with EDTA[1]. The cobalt was determined by the addition of an excess but known volume of standard EDTA solution, and back-titration with a standard cobalt solution. The end-point was indicated by the appearance, in the chloroform layer, of the blue colour of the ion-association pair triphenylmethyl-arsonium tetrathiocyanato cobaltate(II).

In the present paper, this method has been extended to the determination of the metals copper, nickel, iron, chromium and vanadium which, like cobalt, form coloured EDTA complexes. The extractive method possesses advantages, as described in the first paper[1]; these advantages are particularly significant in the case of chromium.

Copper, nickel and iron have been determined by the back-titration of excess EDTA with standard cobalt solution using thiocyanate as indicator, the titration being carried out in a 1:1 acetone–water mixture[2]. Ether has been used to assist the observation of the end-point in the titration of iron(III) with EDTA using thiocyanate as indicator[3,4]. Chromium(III) and vanadium(IV) have been determined by the back-titration of excess EDTA with various metal solutions, using appropriate indicators; for example, manganous sulphate with Eriochrome Black T indicator[5].

APPARATUS AND REAGENTS

The flask used for the titrations has already been described[1].

Solutions used

(A.R. quality reagents were used wherever possible).

Standard EDTA solution. A 0.01 M solution of the disodium salt. This solution was standardised against zinc solution using Eriochrome Black T as indicator.

Standard cobalt(II) solution. A 0.01 M solution of iron-free cobalt ammonium sulphate.

Buffer solutions. (a) pH = 9.3. Concentrated (d = 0.880) aqueous ammonia (150 ml) and ammonium chloride (160 g) made up to 1 l with water. (b) pH = 8.5. Concentrated (d = 0.880) aqueous ammonia (50 ml) and ammonium chloride (215 g) made up to 1 l with water.

Ammonia, approx. 1 M. Potassium thiocyanate (50%). Triphenylmethylarsonium chloride (1%).

Solutions were prepared using distilled water which had been passed through a column containing cation exchange resin in the sodium form. Polythene containers were used for storage.

PROCEDURE

The sample metal ion solution (nickel(II), copper(II), iron(III), chromium(III) or vanadium(IV)) and 25 ml of standard EDTA solution (50 ml for chromium) are pipetted into the titration flask. The sample solution should contain from 2 to 12 mg of nickel or copper, or from 2 to 10 mg of iron, chromium or vanadium*. (If chromium is being estimated, the acid solution must be boiled for at least 5 min after the addition of EDTA to ensure complete complex formation). If necessary, ammonia is added until litmus paper just turns blue. Approximately 10 ml of chloroform are then added, followed by 2 ml of the appropriate buffer solution, 5 ml of potassium thiocyanate solution and 3 ml of triphenylmethylarsonium chloride solution. Buffer solution (*a*) (pH = 9.3) is used for nickel and copper, and solution (*b*) (pH = 8.5) for iron, chromium and vanadium. The excess EDTA is then back-titrated using standard cobalt solution as titrant. The cobalt solution should be added dropwise as the end-point is approached, the flask being stoppered and shaken after the addition of each drop. The end-point is indicated by the appearance of a blue colour in the chloroform layer.

RESULTS

The metal content of different volumes of a solution of known concentration was determined for each of the metals (Tables I to V). With the exception of the first group of results in Table I, which were obtained by determining a smaller quantity

TABLE I

mg of Ni added	mg of Ni found	% Deviation from Ni added	Mean mg of Ni found	% Deviation of mean from Ni added	Maximum % deviation of Ni found from mean
1.256	1.294	+3.0			
1.256	1.287	+2.5			
1.256	1.269	+1.0	1.277	+1.7	1.3
1.256	1.263	+0.6			
1.256	1.269	+1.0			
3.141	3.149	+0.3			
3.141	3.137	—0.1			
3.141	3.143	+(<0.1)	3.151	+0.3	0.5
3.141	3.161	+0.6			
3.141	3.167	+0.8			
6.281	6.298	+0.3			
6.281	6.280	—(<0.1)			
6.281	6.274	—0.1	6.291	+0.2	0.3
6.281	6.298	+0.3			
6.281	6.304	+0.4			

* For the estimation of greater quantities of the metals than those quoted, more EDTA solution should be added, or the concentrations of both EDTA and the standard cobalt solution should be increased. The sample volume should not be more than 150 ml for the quantities of buffer potassium thiocyanate and triphenylmethylarsonium chloride specified. For larger sample volumes, more of these reagents should be used.

of nickel than that recommended in the procedure, it can be seen that the mean value of metal determined may normally be expected to be within 0.5% of the true value, while the maximum variation about this mean is also of the same order, thus leading to a maximum expected error of about 1% for any single determination. One observes in fact that, neglecting the first group of nickel results, the error exceeds 1% in only two of the seventy estimations.

TABLE II

mg of Cu added	mg of Cu found	% Deviation from Cu added	Mean mg of Cu found	% Deviation of mean from Cu added	Maximum % deviation of Cu found from mean
3.211	3.188	—0.7			
3.211	3.201	—0.3			
3.211	3.175	—1.1	3.183	—0.9	0.6
3.211	3.182	—0.9			
3.211	3.169	—1.3			
6.421	6.422	+(<0.1)			
6.421	6.396	—0.4			
6.421	6.409	—0.2	6.409	—0.2	0.2
6.421	6.396	—0.4			
6.421	6.422	+(<0.1)			
12.84	12.79	—0.4			
12.84	12.79	—0.4			
12.84	12.78	—0.5	12.78	—0.5	0.1
12.84	12.79	—0.4			
12.84	12.77	—0.5			

TABLE III

mg of Fe added	mg of Fe found	% Deviation from Fe added	Mean mg of Fe found	% Deviation of mean from Fe added	Maximum % deviation of Fe found from mean
2.835	2.853	+0.6			
2.835	2.841	+0.2			
2.835	2.836	+(<0.1)	2.848	+0.5	0.6
2.835	2.864	+1.0			
2.835	2.847	+0.4			
5.669	5.712	+0.8			
5.669	5.712	+0.8			
5.669	5.689	+0.4	5.699	+0.5	0.5
5.669	5.712	+0.8			
5.669	5.671	+(<0.1)			
11.34	11.40	+0.5			
11.34	11.37	+0.3			
11.34	11.37	+0.3	11.38	+0.4	0.2
11.34	11.40	+0.5			
11.34	11.38	+0.4			

DISCUSSION

The suggested pH at which the titration is to be commenced is 9.3 in the case of nickel and copper, and 8.5 for iron, chromium and vanadium. It was found that the solution

TABLE IV

mg of Cr added	mg of Cr found	% Deviation from Cr added	Mean mg of Cr found	% Deviation of mean from Cr added	Maximum % deviation of Cr found from mean
2.593	2.609	+0.6			
2.593	2.599	+0.2			
2.593	2.588	—0.2	2.597	+0.2	0.5
2.593	2.604	+0.4			
2.593	2.583	—0.4			
5.186	5.234	+0.9			
5.186	5.218	+0.6			
5.186	5.192	+0.1	5.217	+0.6	0.5
5.186	5.228	+0.8			
5.186	5.213	+0.5			
10.37	10.43	+0.6			
10.37	10.41	+0.4			
10.37	10.38	+0.1	10.41	+0.4	0.3
10.37	10.44	+0.7			
10.37	10.39	+0.2			

TABLE V

mg of V added	mg of V found	% Deviation from V added	Mean mg of V found	% Deviation of mean from V added	Maximum % deviation of V found from mean
2.550	2.551	+(<0.1)			
2.550	2.546	—0.2			
2.550	2.546	—0.2	2.545	—0.2	0.4
2.550	2.536	—0.5			
2.550	2.546	—0.2			
5.099	5.101	+(<0.1)			
5.099	5.112	+0.3			
5.099	5.117	+0.4	5.111	+0.2	0.2
5.099	5.117	+0.4			
5.099	5.107	+0.2			
10.20	10.22	+0.2			
10.20	10.20	0.0			
10.20	10.21	+0.1	10.20	0.0	0.2
10.20	10.19	—0.1			
10.20	10.19	—0.1			

could be at least 0.5 pH units above or 1.0 pH unit below these values without affecting the results. The pH variations which could be encountered in practice would be well within this range.

The range of volumes of potassium thiocyanate, triphenylmethylarsonium chloride and buffer solutions giving a titration deviating by no more than 0.1 ml from the normal result have been found for the cobalt determination[1]. These volumes (KSCN, 1 to 30 ml; Ph₃MeAsCl, 1 to 30 ml; and buffer, 0.5 to 8 ml) again gave an error no greater than 0.1 ml in the titrations involved in the present metal determinations with one exception only. This occurred in the case of copper(II), where 8 ml of buffer solution gave a high titration result; however, reduction to 7 ml reduced the titration

error to 0.1 ml. This effect may be attributed to the ammonia in high concentration competing with the EDTA as a complexing agent for the copper.

After the addition of excess EDTA to the metal solution, the resulting solution should, if necessary, be first neutralised with ammonia. The chloroform and other reagents may then be added in any order without affecting the result of the titration. Ammonia, if added before the EDTA, may interfere with the determination by precipitating the metal hydroxide. Again, if thiocyanate is added before the EDTA to the copper(II) solution, partial reduction to copper(I) occurs, thus giving a low result for the copper determination.

When quantities of chromium near the upper limit of the specified range (10 mg) were determined, 25 ml of EDTA provided an insufficient excess, for even after boiling the solution for 20 min all of the chromium was not complexed. Accordingly, 50 ml of EDTA has been recommended in the procedure for chromium.

For the determination of quantities of metals of the order of ten times those specified in the procedure, 0.1 M solutions of cobalt and EDTA may be used and very sharp end-points are still obtained, provided that more buffer is used. On the other hand, if one attempts to determine similar quantities of the metals with 0.1 M solutions by ordinary methods (for nickel and copper, direct titration with EDTA using murexide as indicator; for iron, direct titration using Variamine Blue indicator; for chromium and vanadium, back-titration with standard zinc solution using Eriochrome Black T as indicator) comparable results are obtained for nickel, copper and iron, but in the case of vanadium the end-point is very diffuse, and with chromium, the end-point can not be seen at all, due to the intensity of colour of the solution. Hence, it may be seen that the extractive end-point method is more widely applicable to coloured solutions than methods in which the end-point is observed in the aqueous phase.

SUMMARY

A method for the determination of nickel, copper, iron, chromium and vanadium by the addition of excess EDTA and back-titration with standard cobalt solution is recommended. The titration involves an extractive method of end-point detection, depending on the appearance of the blue colour of the ion-association pair $[Ph_3MeAs]_2[Co(SCN)_4]$ in chloroform. The method is therefore suitable for the determination of these metals in highly coloured aqueous solutions. The maximum expected error is of the order of 1%, and in the majority of determinations the error is 0.5% or less.

RÉSUMÉ

Une méthode est proposée pour le dosage du nickel, du cuivre, du fer, du chrome et du vanadium par addition d'EDTA en excès et titrage en retour au moyen d'une solution étalon de cobalt. La détection du point final se fait par extraction dans le chloroforme du composé bleu $[Ph_3MeAs]_2$ $[Co(SCN)_4]$, permettant ainsi un dosage même dans des solutions fortement colorées.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Nickel, Kupfer, Eisen, Chrom und Vanadium. Die Lösung wird mit Chloroform, einem Überschuss von EDTA, Kaliumthiocyanat und Triphenyl-arsoniumchlorid versetzt und der Überschuss an EDTA mit einer Kobaltlösung zurücktitriert. Der Endpunkt wird durch das Auftreten der blauen Farbe des $[Ph_3MeAs]_2\,Co(SCN)_4]$ in der Chloroformschicht angezeigt.

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DOSAGE OXYDIMÉTRIQUE DE L'ACIDE URIQUE PAR L'IODATE ET LE PERIODATE DE POTASSIUM

A. BERKA

Institut de chimie analytique, Université Charles, Prague (Tchécoslovaquie)

(Reçu le 27 février 1961)

On a proposé pour le dosage volumétrique de l'acide urique toute une série d'agents oxydants qui permettent de le déterminer par titrage direct ou par rétitration de l'agent en excès. On utilise notamment des solutions étalons d'iode[1-3], de permanganate de potassium[4], de sulfate de cérium[5], de chloramine T[6], de vanadate de sodium[7], de bromate de potassium en présence d'un bromure[3], de ferricyanure alcalin[8] ou le réactif de Fehling[9].

Nous avons étudié l'oxydation de l'acide urique par l'iodate et le periodate et constaté que la réaction avec ces réactifs s'effectue, dans les solutions convenablement acidifiés par l'acide chlorhydrique, si rapidement, que l'on peut l'utiliser pour un dosage potentiométrique direct. La concentration de l'acide chlorhydrique a une influence non seulement sur la vitesse, mais encore sur l'évolution stoichiométrique de la réaction.

PARTIE EXPÉRIMENTALE

Réactifs

La solution d'acide urique est préparée par dissolution de 1.68 g de produit pur dans 200 ml d'eau distillée bouillante, contenant 1 g de carbonate de lithium, et complétée à un volume de 1000 ml par de l'eau distillée. Le titre a été contrôlé chaque jour par iodométrie[3]. Solution de iodate de potassium (p.a. Merck) 0.01 M. Solution de periodate de potassium (purrum Lachema) 0.01 M, titreé avec du sulfate d'hydrazine[10].

Appareils

Les titrages potentiométriques ont été effectués au moyen d'un pH-mètre EK/21 (Kovodružba, Praha) en utilisant un fil de platine comme électrode indicatrice et une électrode au calomel comme électrode de référence. Le liquide était agité par un dispositif électromagnétique. Les titrages ont été effectués à l'aide d'une microburette de 5 ml (graduées en 0.01 ml).

RÉSULTATS

Par la plupart des agents, l'acide urique est oxydé (en milieu acide) en formant l'alloxane et l'urée, d'après l'équation:

$$\begin{array}{l} \text{NH—CO} \\ |\quad\ \ | \\ \text{CO}\quad \text{C—NH} \\ |\quad\ \ \| \qquad\qquad \text{CO} \\ \text{NH—C—NH} \end{array} + 1/2\ O_2 + H_2O \rightarrow \begin{array}{l} \text{NH—CO}\qquad \text{NH}_2 \\ |\quad\ \ | \qquad\qquad | \\ \text{CO}\quad \text{CO}\ +\ \text{CO} \\ |\quad\ \ | \qquad\qquad | \\ \text{NH—CO}\qquad \text{NH}_2 \end{array} \qquad (1)$$
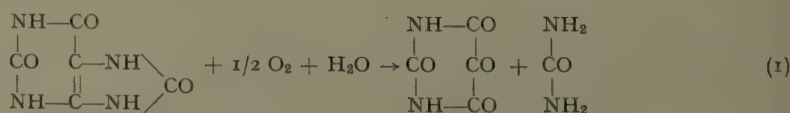
La réduction de l'iodate et du periodate dans les solutions chlorhydriques s'effectue en fonction de la concentration de l'acide chlorhydrique et selon la nature de l'oxydant d'après le schéma.

$$IO_3^- + 6 H^+ + 6 e \rightarrow I^- + 3 H_2O \tag{2a}$$

$$IO_4^- + 8 H^+ + 8 e \rightarrow I^- + 4 H_2O \tag{2b}$$

$$2 IO_3^- + 12 H^+ + 10 e \rightarrow I_2 + 6 H_2O \tag{3a}$$

$$2 IO_4^- + 16 H^+ + 14 e \rightarrow I_2 + 8 H_2O \tag{3b}$$

$$IO_3^- + 6 H^+ + 4 e \rightarrow I^+ + 3 H_2O \tag{4a}$$

$$IO_4^- + 8 H^+ + 6 e \rightarrow I^+ + 4 H_2O \tag{4b}$$
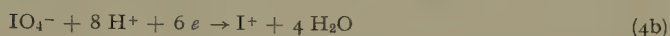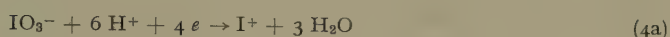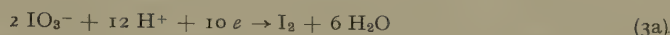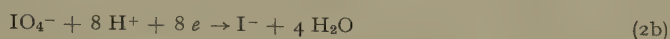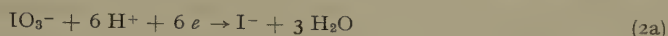
Pour cette raison nous avons étudié, par titrage potentiométrique direct, l'influence de la concentration de l'acide sur l'évolution stoichiométrique de la réaction de l'acide urique avec l'iodate et avec le periodate.

Titrage de l'acide urique par l'iodate de potassium

Au cours de ces expériences nous avons titré, dans des solutions différemment acidifiées par l'acide chlorhydrique, 15 mg d'acide urique par une solution d'iodate de potassium 0.01 M dans un volume initial de 50 ml. Nous avons constaté, que dans
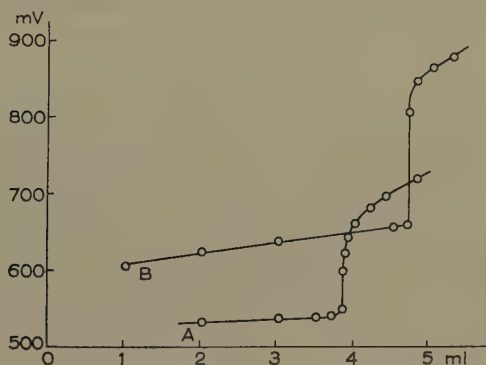
Fig. 1. Titrage de 15 mg d'acide urique par l'iodate de potassium, (A) dans un milieu de HCl à 0.8% (réduction en I_2), (B) dans un milieu de HCl à 15% (réduction en ICl).

les solutions contenant 0.4–1.5% de HCl l'oxydation de l'acide urique s'effectue d'après l'éqn. (1), et l'iodate est réduit quantitativement en iode élémentaire (3a). Sur la courbe potentiométrique l'achèvement de la réaction est marqué par une variation brusque du potentiel (voir Fig. 1, courbe A). Les solutions, initialement blanc trouble par la présence de l'acide urique, se clarifient au cours du titrage et se colorent par l'iode. Au voisinage de l'équivalence, il est nécessaire d'attendre 2 min pour que le potentiel se stabilise. L'équivalence étant atteinte, le réactif en excès oxyde l'iode en chlorure de iode. La couleur du iode disparaît, sans que le potentiel change visiblement.

Dans les solutions neutres ou très peu acidifiées par HCl, la réaction de l'acide urique avec l'iodate ne s'effectuait pas assez rapidement pour qu'on puisse la suivre par titrage potentiométrique. En diminuant la concentration de l'acide chlorhydrique au-dessous de 1.5%, la variation du potentiel correspondant à la réduction de l'iodate en iode devenait de moins en moins nette jusqu'à sa disparition complète.

Une réduction quantitative et immédiate de l'oxydant en chlorure de iode (éqn. 4a) s'effectue au cours du titrage de l'acide urique (éqn. 1) dans les solutions d'acide chlorhydrique à 11–30%. La variation du potentiel au point équivalent est encore plus nette (Fig. 1, courbe B) que dans le cas de la réduction de l'iodate en iode. Le titrage peut être effectué même avec une concentration de HCl plus grande, mais il est nécessaire alors d'attendre un certain temps la stabilisation du potentiel au voisinage du point équivalent. Quand la concentration de l'acide chlorhydrique est inférieure à 11% les résultats dépendent de la vitesse du titrage et ils comportent une erreur positive.

Pour le dosage de l'acide urique il est donc possible d'utiliser le milieu HCl soit à 0.4–1.5% soit à 11–30%. Nous avons déterminé de cette manière de 8–60 mg d'acide urique dans un volume de 50 ml. La différence relative moyenne, calculée chaque fois d'après 10 dosages, était dans le premier cas de 0.14% et dans le deuxième de 0.11%. La variation du potentiel sur 0.02 ml d'oxydant 0.01 M est dans HCl à 0.8% de 50 mV, dans HCl à 15% de 150 mV. Le potentiel au point d'inflexion est aux environs de 580 mV dans le premier milieu et 740 mV dans le second. 1 ml de KIO$_3$ 0.01 M correspond resp. à 4.20275 et 3.3622 mg d'acide urique.

La stabilisation immédiate du potentiel et l'importance de sa variation au point équivalent amènent à recommander à des fins analytiques le milieu HCl à 11–30%.

Titrage de l'acide urique par le periodate de potassium

Afin de voir si le periodate de potassium (dont nous avons étudié précédemment l'utilisation en analyse volumétrique[11]) réagit avec l'acide urique de la même manière que l'iodate, nous avons effectué avec ce réactif les mêmes essais qu'avec l'iodate.

Nous avons constaté que la réduction du periodate en chlorure d'iode (éqn. 4b) s'effectue quantitativement avec la même vitesse et dans les mêmes conditions qu'avec l'iodate. Pendant le titrage potentiométrique de l'acide urique en solution
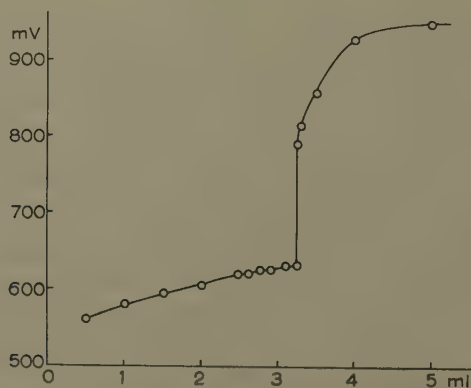
Fig. 2. Titrage de 15 mg d'acide urique par le periodate de potassium dans un milieu de HCl à 15%.

HCl à 11–30% (voir Fig. 2), le potentiel (pendant tout le titrage) se stabilise immédiatement; au point équivalent la variation du potentiel est de 160 mV sur 0.02 ml d'oxydant 0.01 M, le potentiel au point d'inflexion est aux environs de 720 mV (en HCl à 15 %). En dosant de 8 à 60 mg d'acide urique la différence relative moyenne (calculée sur dix mesures) était de 0.12%. 1 ml de KIO$_4$ 0.01 M correspond à 5.0433 mg d'acide urique.

Le titrage direct de l'acide urique dans les solutions de HCl de concentration inférieure ne conduisait jamais (contrairement au cas de l'iodate) à la réduction du periodate en iode. La présence d'iode élémentaire a pu être qualitativement mise en évidence seulement après une action prolongée du réactif en excès.

RÉSUMÉ

Il est possible de doser l'acide urique par un titrage potentiométrique direct au moyen d'une solution d'iodate ou de periodate de potassium, dans des solutions acidifiées de manière appropriée par l'acide chlorhydrique. Selon la concentration de HCl le réactif est réduit en chlorure d'iode, ou en iode élémentaire (dans le cas de l'iodate).

SUMMARY

Uric acid is determined by potentiometric titration with potassium iodate or periodate in solutions containing hydrochloric acid. Depending on the acid concentration the reagent is reduced to iodine monochloride, or to elementary iodine (in the case of iodate).

ZUSAMMENFASSUNG

Harnsäure kann durch potentiometrische Titration mit Kalium-Jodat oder -Perjodat in Lösungen, die mit Chlorwasserstoffsäure geeignet angesäuert sind, bestimmt werden. Der Konzentration der Chlorwasserstoffsäure entsprechend wird das Reagens zu Jodmonochlorid, bzw. zu elementarem Jod (im Falle von Jodat) reduziert.

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APPLICATION OF SELENIUM SALTS IN INORGANIC ANALYSIS

I. K. TAIMNI AND RAM RAKSHPAL

Chemical Laboratories, University of Allahabad (India)

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Several papers[1,2] have appeared from this laboratory dealing with the application of thio salts in qualitative and quantitative analysis. In view of the strong similarity of selenium to sulphur and the analogous reactions of their salts, the behaviour of the selenium salts has now been investigated for the determination of several metals. A general study of the metals which form insoluble sulphides showed that the selenium compounds behave almost exactly like the corresponding sulphur compounds. Those which form thio salts also form soluble seleno salts with excess of sodium selenide and these are decomposed by excess of acid with the complete precipitation of the corresponding selenides. In other cases insoluble selenides are directly precipitated like the sulphides. The main differences between the compounds of sulphur and selenium lie in the greater toxicity of hydrogen selenide and in the greater contamination of the selenide precipitates with the selenium formed by atmospheric oxidation of sodium selenide. If sodium sulphide is prepared below 5° and precipitation is carried out in ice-cold solutions, the oxidation of sodium sulphide with precipitation of sulphur is negligible. But although the oxidation of sodium selenide is reduced at a low temperature, considerable quantities of selenium are still found in the selenide precipitates. Hydrogen selenide is a colourless gas which produces dryness and a pungent and painful sensation on coming in contact with mucous membranes; its smell is similar to hydrogen sulphide. A specially devised apparatus of the type shown below is therefore necessary.

For sodium selenide to be useful for the determination of metals, atmospheric oxidation of sodium selenide must be prevented both in the preparation of the reagent and during its use as a precipitant. Acceptable results can be obtained by maintaining an atmosphere of carbon dioxide or nitrogen in the bottles in which sodium selenide is prepared and the metallic selenides are precipitated provided that care is taken to prevent sodium selenide coming in contact with air. The slightest exposure to air results in contamination with selenium, but this can be removed by washing with carbon disulphide. The precipitated selenide which remains behind can be weighed in a pure form after washing with alcohol and ether successively and drying in a vacuum desiccator.

As an example of what happens when metals are determined as selenides by adopting ordinary precautions to prevent oxidation, arsenic was precipitated as the selenide (As_2Se_5); a positive error of 0.3–0.4% was obtained when 20–45 mg of arsenic was precipitated.

The prevention of oxidation by ordinary methods requires extreme care, hence it

was considered desirable to devise an apparatus (Fig. 1) in which (*a*) the whole pro-
cedure could be carried out without contact with air, (*b*) the hydrogen selenide formed
could be removed without contaminating the surrounding atmosphere and (*c*) the
temperature of the solutions could be maintained between 5–10°.
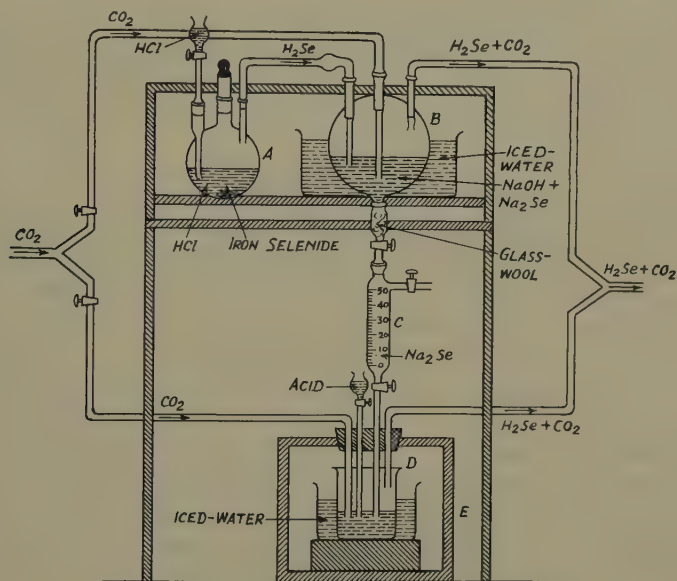
Fig. 1. Apparatus for precipitating selenides.

The following points should be noted with regard to the determination of metals
as selenides:

(*1*) The selenides are precipitated by the addition of excess of acid to seleno salts
without the heating which is necessary for sulphides.

(*2*) Filtration of the selenides is easier than that of sulphides.

(*3*) All selenides can be weighed after washing with distilled water, alcohol and
ether successively and drying in a vacuum desiccator; no heating has been found
necessary so far.

It can be seen, therefore, that the selenides provide a more convenient and quicker
method of determining metals than sulphides.

Obviously, the apparatus described can be employed for the quantitative precipi-
tation of any metal where oxidation by air interferes.

EXPERIMENTAL

Apparatus (see Fig. 1)

Hydrogen selenide is generated in flask A by adding concentrated hydrochloric
acid to ferrous selenide and is passed into the sodium hydroxide solution in flask B,
which is maintained at 5–10° by placing it in iced water. Flask B is fitted with three
tubes: the first to remove air in the flask by passing carbon dioxide, the second to
conduct hydrogen selenide from flask A, and the third to remove the excess of hydro-
gen selenide by means of a long rubber tube which leads out of the laboratory.

The sodium selenide solution is placed in burette C and a measured volume is then added to the beaker D containing the cold metallic salt solution. The beaker is placed in a trough containing iced water within a cabinet E which is also fitted with (*1*) a thistle funnel for adding measured quantities of acid, (*2*) a tube for conducting carbon dioxide into the beaker (which removes air from the cabinet and stirs the solution) and (*3*) a tube for removing the hydrogen selenide formed by the addition of acid to the seleno salts. The whole operation is thus carried out easily without any contact with air until the insoluble selenide has been precipitated and is ready for filtration, washing and weighing.

<div align="center">METHODS</div>

Preparation of hydrogen selenide

Alternate layers of iron filings (obtained by drilling soft iron) and powdered selenium were placed in a Rose crucible which was then heated to 500–650° for about an hour. The resulting cooled mass of ferrous selenide was removed and powdered and a portion was placed in flask A, from which all air had been displaced by carbon dioxide. On adding concentrated hydrochloric acid through the thistle funnel a steady stream of hydrogen selenide was evolved after a few minutes and conducted into flask B.

Preparation of sodium selenide

After flask B had been freed from air by carbon dioxide, 150–200 ml of a 2 *N* sodium hydroxide solution (E. Merck) was introduced and cooled to a temperature of 5–10°. Hydrogen selenide was then passed into this solution for 5–7 min. The hydrogen selenide was evolved slowly and bubbled through the solution in flask B forming sodium selenide. If the temperature of the solution fell below 5° the sodium selenide tended to precipitate as white crystals and clogged the tube leading to burette C. The same thing happened if the concentration of alkali was much above 2 *N*. Some glass wool was placed at the bottom of flask B to catch any solid sodium selenide formed. If the temperature rose much above 10°, the sodium selenide tended to decompose imparting a reddish colour to the solution. A temperature of 5–10° gave the best conditions. The excess of hydrogen selenide, after the preparation of sodium selenide, was removed by passing carbon dioxide through the flask B into the long rubber exit tube.

Precipitation of selenides

A measured volume of the metallic salt sample solution was placed in the beaker D which was cooled to about 10°. After the air in the cabinet had been removed by passing carbon dioxide, a measured volume of the sodium selenide solution was added from burette C (provided with an outlet tube at the top to allow displacement of the carbon dioxide and introduction of sodium selenide). The solution of the seleno salt was stirred for a few seconds with carbon dioxide and a measured volume of hydrochloric acid or acetic acid was then added through a thistle funnel to decompose the seleno salt (if formed) and precipitate the insoluble selenide. The insoluble selenide was quickly and completely precipitated in an easily filterable form without heating. A current of carbon dioxide was then passed into the mixture for stirring and to remove completely the hydrogen selenide evolved. The beaker was then removed from the cabinet, the mixture was filtered through a sintered glass crucible (porosity G 4)

nd the precipitate was washed successively with water, alcohol and ether, sucked
ry for 15 min at the filter pump, dried in a vacuum desiccator for about 30–35 min
nd weighed.

laterials

The materials used in the various determinations were usually obtained from E.
Ierck, B.D.H. (AnalaR), or Kahlbaum, and the solutions prepared were carefully
andardized by reliable methods.

It was considered desirable to make a thermogravimetric study of the selenides
recipitated in order to obtain definite information regarding the correct conditions
or weighing. The results so obtained are described below. A standard Stanton
hermobalance was used; details of its working have been given previously[3]. The
eagents used and the methods followed in preparing precipitates for thermogravi-
etric studies were the same as in the gravimetric determination.

Determination of elements

rsenic

Solutions of sodium arsenate were prepared and standardized by Volhard's method[4]
by the sodium sulphide method[2]. Aliquots of the solutions were then treated with
xcess of the freshly prepared 2 N sodium selenide solution, about 25 ml of the alkali
lenide solution being required for every 50 mg of arsenic. The clear solution was then
eated with sufficient hydrochloric acid (12 N) to neutralize the alkali and to give
final concentration of approximately 6 N hydrochloric acid. The mixture was left
the ice-cold water and stirred thoroughly with carbon dioxide. The precipitate of
rsenic selenide, brick-red in colour, was then filtered and treated as in the above
eneral method. The weight of the precipitate corresponded to the formula As_2Se_5.
some experiments the precipitate of arsenic selenide was also washed with carbon
sulphide but there was no change in weight, which shows that no precipitation of
ee selenium occurred.

Typical results obtained by this procedure are shown in Table I.

The air-dried sample of arsenic pentaselenide gave a horizontal level up to 410°.
om this temperature the selenide began to sublime and the sublimation was com-

TABLE I

WITH 2 N SODIUM SELENIDE REAGENT

Arsenate solution (ml)	Reagent added (ml)	12 N HCl added (ml)	Weight of ppt. As_2Se_5 (g)	As found (g)	As present (g)
25	35	45	0.2512	0.06908	
25	40	55	0.2513	0.06911	0.06903
25	35	50	0.2512	0.06908	
20	18	25	0.1280	0.03521	
20	20	30	0.1280	0.03521	0.03520
20	20	35	0.1281	0.03523	
10	15	20	0.1003	0.02758	
10	15	20	0.1003	0.02758	0.02754
10	10	15	0.1002	0.02755	

pleted at 550°. At this temperature the crucible was found to be empty (Fig. 2).

Tin

A pure sample of metallic tin was dissolved in concentrated hydrochloric acid and oxidized with bromine and the solution of stannic chloride was standardized by the cupferron[5], ammonia[4] or the sodium sulphide method[1]. Aliquots of this solution were
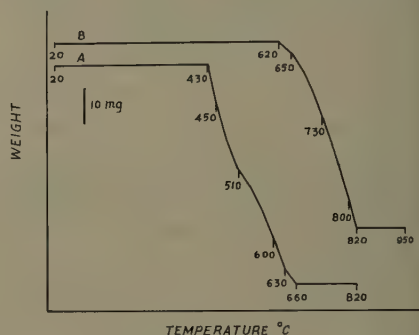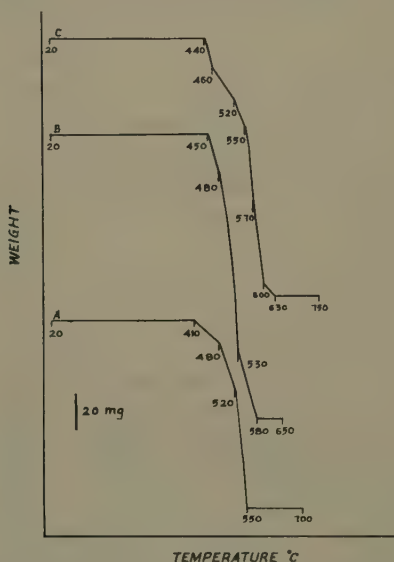
Fig. 3. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, antimony pentaselenide; B, silver selenide.

Fig. 2. Thermal decomposition curves of selenides precipitated by sodium selenide reagent. A, arsenic pentaselenide; B, rhenium heptaselenide; C, mercuric selenide.

treated with ammonium hydroxide until a white precipitate of stannic hydroxide appeared and then with excess of the selenide reagent. This gave a brownish-yellow solution of sodium seleno-stannate, which was then decomposed by excess of 4 N hydrochloric acid to form a reddish brown precipitate. The mixture was cooled in ice-cold water and the precipitate of tin selenide filtered and treated as in the general method. The weight of the precipitate corresponded to the formula $SnSe_2$.

The solution of sodium seleno-stannate should be decomposed with sufficient 4 N hydrochloric acid to give a final acidity of 1–2 N. If more acid is used the precipitate tends to pass through the filter.

Antimony

A solution of potassium hydrogen antimonate was prepared and standardized by reduction with mercury[6] and titration with potassium bromate[7] or by the sodium sulphide method[2]. Aliquots of this solution were treated with the selenide reagent and the seleno salt formed was decomposed with an excess of 4 N hydrochloric acid. The mixture was then cooled and the brown precipitate of antimony selenide was filtered, and treated as in the general procedure. The weight of the precipitate corresponded to the formula Sb_2Se_5.

Antimony cannot be determined as selenide from antimony potassium tartrate solution, because sodium selenide forms metallic selenium with sodium tartrate.

An air-dried sample of antimony pentaselenide gave a horizontal up to 430° and

en lost weight. The loss was complete at 660° and a horizontal was obtained beyond
50° corresponding to Sb_2O_4. The antimony formed by the decomposition of the
entaselenide was oxidized immediately to Sb_2O_4. The behaviour of antimony selenide
herefore corresponded to that of the sulphide[3] (Fig. 3).

latinum

Solutions of platinic chloride were standardized by reduction to metal with formic
cid[8] or by the sodium sulphide method[2]. Aliquots were neutralized with a cold
odium hydroxide solution and treated with the selenide reagent. The solution con-
ining the seleno salt was acidified with a large excess of acetic acid, stirred well with
arbon dioxide, cooled in iced water and treated with about 5 g of ammonium acetate.
f hydrochloric acid was used instead of acetic acid the precipitate tended to pass
rough the filter). The black precipitate of platinum selenide was filtered at a low
ressure and treated as in the general procedure. The ratio of the weight of the metal
that of the precipitated selenide was always found to be 0.4403 which corresponds
xactly to the formula $PtSe_2 \cdot 5 H_2O$.

An oven-dried sample of platinum selenide lost weight from 220° to 500°. From
00° to 700° there was a horizontal corresponding to the weight of the metal (Fig. 4).
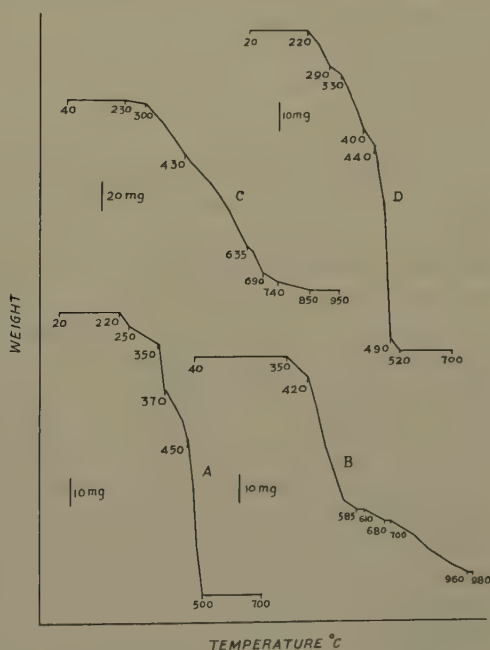
g. 4. Thermal decomposition curves of
lenides precipitated by sodium selenide
agent. A, platinum selenide; B, palladium
lenide; C, rhodium selenide; D, ruthenium
selenide.

uthenium

Ruthenium can be precipitated as metal[9] from an alkaline solution by boiling with
cohol. The precipitated metal is ignited and cooled in a current of hydrogen and
eighed. If ruthenium selenide is precipitated by treating the solution with sodium
lenide and acetic acid successively it can be weighed directly after washing with
cohol and ether, and the whole determination is completed in about 3 h.

Solutions were prepared and standardized by the sodium sulphide method[2]. Aliquots of the solution were made slightly alkaline with a cold solution of sodium hydroxide, then treated with a large excess of the selenide reagent followed by acetic acid in excess and about 10 g of ammonium acetate. The precipitate was then treated as usual. The ratio of the weight of the metal to that of the precipitate was always found to be 0.4267 which corresponds exactly to the formula $Ru_2Se_3 \cdot 2 H_2O$.

An oven-dried sample of ruthenium selenide lost weight from 220° to 520°. From 520° to 700° there was a horizontal which corresponded to the weight of the metal. Because of spurting, the experiment was carried out in a partly covered crucible (Fig. 4).

Palladium

Solutions of palladium chloride were prepared in dilute hydrochloric acid and standardized by the dimethylglyoxime method[10] or the sodium sulphide method[2]. Aliquots were neutralized with ammonium hydroxide and treated with the selenide reagent. The determination was then completed as for platinum. The weight of the black precipitate of palladium selenide corresponds to the formula $PdSe$.

The air-dried sample of palladium selenide gave a horizontal up to 350° and then lost weight. There were two horizontals from 585° to 610° and 680° to 700°. These horizontals did not correspond to any exact formula. The loss in weight continued up to 960° after which there was a horizontal up to 980° corresponding to the weight of the metal (Fig. 4).

Rhodium

In all the known methods for the determination of rhodium, except the sodium sulphide method[2], the precipitate must be ignited and cooled in a current of hydrogen before being weighed. A careful study of the behaviour of rhodium salts with sodium selenide and acetic acid has shown that the precipitate of the selenide, after suitable treatment, can be weighed directly.

A solution was prepared by dissolving rhodium chloride in dilute hydrochloric acid and standardized by the formic acid method[11] or by the sodium sulphide method[2]. The determination as selenide was done in the same way as for palladium. The ratio of the weight of the metal to that of the precipitate was always found to be 0.3001 which corresponds exactly to the formula $Rh_2Se_3 \cdot 3 H_2Se$.

The air-dried sample of rhodium selenide gave a horizontal up to 230° and lost weight from 230° to 850°. From 850° to 950° there was a horizontal corresponding to the weight of the metal. Because of slight spurting, the experiment was carried out in a partly covered crucible (Fig. 4).

Rhenium

Rhenium forms, on treatment with sodium sulphide, a thio salt[2] which decomposes on acidification to precipitate the heptasulphide. Similarly, rhenium forms, on treatment with sodium selenide, a seleno salt which decomposes on acidification to yield heptaselenide. Treatment with acetic acid and ammonium acetate fails to decompose the seleno salt completely and gives low results, but treatment with excess of concentrated hydrochloric acid is satisfactory.

A solution of perrhenate was standardized by the sulphide–nitron method[12] or the

sodium sulphide method[2]. Aliquots were treated with the selenide reagent, followed by a large excess of 12 N hydrochloric acid. The selenide was completely precipitated without heating (unlike sulphide[2]) and the precipitate settled easily on cooling in ice-cold water. The black precipitate of the selenide was filtered, washed, dried and weighed as in the case of platinum. Its weight corresponded to the formula Re_2Se_7.

The air-dried sample of rhenium heptaselenide gave a horizontal up to 450°. There was a steady loss in weight from 450° to 580° and at 580° the crucible was found to be empty (Fig. 2).

Mercury

Solutions of mercuric chloride were standardized by VOLHARD's method[13] or by the sodium sulphide method[2]. Aliquots were treated with ammonium hydroxide until a slight turbidity appeared and then with an excess of the selenide reagent. The formation of the seleno salt of mercury with sodium selenide required a large excess of reagent and vigorous shaking. The mixture was acidified with 6 N hydrochloric acid (final acidity 3 N) and cooled in ice-water. The black precipitate of mercuric selenide was then filtered and treated as in the general procedure. Its weight corresponded to the formula HgSe.

The air-dried sample of mercuric selenide was stable up to 440°. A rapid loss in weight then ensued up to 630° when the crucible was found to be empty (Fig. 2).

TABLE II

DETERMINATION OF METALS AS SELENIDES

Metal	Amount of metal (g)	Error %
Arsenic	0.0690–0.0176	+0.03–+0.20
Antimony	0.0693–0.0181	+0.03–+0.20
Tin	0.0783–0.0250	+0.05–+0.30
Platinum	0.0420–0.0105	+0.05–+0.35
Palladium	0.0628–0.0230	+0.10–+0.30
Rhodium	0.0285–0.0072	+0.07–+0.35
Ruthenium	0.0592–0.0148	+0.06–+0.25
Rhenium	0.0347–0.0131	+0.10–+0.35
Mercury	0.1479–0.0300	+0.06–+0.30
Silver	0.0874–0.0262	+0.04–+0.25
Gold	0.0595–0.0149	+0.02–+0.10

TABLE III

METAL SULPHIDES AND SELENIDES FORMED

Salt	Arsenic	Antimony	Tin	Rhenium	Mercury	Silver	Platinum	Palladium	Rhodium	Gold	Ruthenium
Thio salt	As_2S_5	Sb_2S_5	$SnS_2 \cdot$ 2 H_2O	Re_2S_7	HgS	Ag_2S	$PtS_2 \cdot$ 5 H_2O	$PdS \cdot$ 2 H_2O	$Rh_2S_3 \cdot$ 3 H_2S	Au_2S_3	$Ru_2S_3 \cdot$ 2 H_2O
Seleno salt	As_2Se_5	Sb_2Se_5	$SnSe_2$	Re_2Se_7	HgSe	Ag_2Se	$PtSe_2 \cdot$ 5 H_2O	PdSe	$Rh_2Se_3 \cdot$ 3 H_2Se	Au_2Se_3 $\cdot H_2Se$	$Ru_2Se_3 \cdot$ 2 H_2O

Silver

Solutions of silver nitrate were standardized by VOLHARD's method[11] or by weighing as silver chloride[14]. Aliquots were treated with ammonium hydroxide until a clear

solution was obtained, and then with an excess of the selenide reagent, stirred well and cooled in ice-cold water. The brownish-black precipitate was filtered and treated as in the general procedure. The weight corresponded to the formula Ag_2Se.

The air-dried sample of silver selenide gave a horizontal up to 620°. A rapid loss in weight followed up to 820°. The horizontal from 820° corresponded to the weight of the metal (Fig. 3).

Gold

The well-known method for the gravimetric determination of gold depends on reduction and weighing as the metal. The reduction method takes 6–12 h, depending on the reducing agent used; the method described below requires 3 h and gives results which are as accurate as those obtained by reduction.

Solutions were standardized by precipitating the metal either with sulphur dioxide[15] in an acid medium or with hydrogen peroxide[11] in an alkaline medium. Aliquots were made alkaline with a cold solution of sodium hydroxide, treated with the selenide reagent and shaken thoroughly. An excess of 6 N hydrochloric acid was then added and the black selenide was treated as in the general procedure. The ratio of the weight

TABLE IV

Weight of Ag_2Se taken (mg)	Weight of Ag calculated (820°–950°) (mg)	Weight of Ag from graph (820°–950°) (mg)
190	140	140
427	313	312
118	57	56
232	112	110

Weight of $PtSe_2 \cdot 5 H_2O$ taken (mg)	Weight of Pt calculated (500°–700°) (mg)	Weight of Pt from graph (500°–700°) (mg)
315	139	140
165	72	73

Weight of PdSe taken (mg)	Weight of Pd calculated (960°–980°) (mg)	Weight of Pd from graph (960°–980°) (mg)
200	115	116
213	123	124

Weight of $Ru_2Se_3 \cdot 2 H_2O$ taken (mg)	Weight of Ru calculated (520°–700°) (mg)	Weight of Ru from graph (520°–700°) (mg)
194	83	81
162	69	67

Weight of $Rh_2Se_3 \cdot 3 H_2Se$ taken (mg)	Weight of Rh calculated (850°–950°) (mg)	Weight of Rh from graph (850°–950°) (mg)
216	65	66
197	59	60

f the metal to that of the precipitate was found to be 0.5538 which corresponds xactly to the formula $Au_2Se_3 \cdot H_2Se$.

The amounts of metal involved in the determinations and the percentage errors are hown in Table II. The compounds formed by sulphides and selenides in the case of ifferent metals are given in Table III for comparison.

The thermogravimetric studies showed that the precipitates of As_2Se_5, Re_2Se_7 and IgSe sublime at a particular temperature, while Sb_2Se_5 is converted to Sb_2O_4 and .g$_2$Se, $PtSe_2 \cdot 5 H_2O$, PdSe, $Rh_2Se_3 \cdot 3 H_2Se$ and $Ru_2Se_3 \cdot 2 H_2O$ are converted to their netals (as in the case of the corresponding sulphides[3]).

The weights calculated and those actually obtained on heating Sb_2Se_5, Ag_2Se, $PtSe_2 \cdot$ H$_2$O, PdSe, $Rh_2Se_3 \cdot 3 H_2Se$ and $Ru_2Se_3 \cdot 2 H_2O$ are given in Table IV.

SUMMARY

he gravimetric determination of metals as selenides is proposed. Owing to the rapid atmos-heric oxidation of sodium selenide and the toxic nature of hydrogen selenide, special apparatus required. The methods are analogous to precipitation of sulphides. Arsenic, tin, antimony, latinum, ruthenium, palladium, rhodium, rhenium, mercury, silver and gold can be determined. he thermolysis of precipitates formed with arsenic, antimony, mercury, silver, rhenium, platinum, uthenium, palladium and rhodium has been studied.

RÉSUMÉ

es auteurs ont effectué une étude sur le dosage gravimétrique de métaux sous forme de séléniures. 'arsenic, l'étain, l'antimoine, le platine, le ruthénium, le palladium, le rhodium, le rhénium, le ercure, l'argent et l'or ont pu être ainsi dosés.

ZUSAMMENFASSUNG

eschreibung einer Untersuchung über die gravimetrische Bestimmung von Arsen, Antimon, Zinn, latin, Ruthenium, Palladium, Rhodium, Rhenium, Quecksilber, Silber und Gold als Selenide nd das thermolytische Verhalten dieser Selenide.

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ELIMINATION OF DISTILLATION IN THE KJELDAHL METHOD FOR THE MICRO- AND SEMIMICRO-DETERMINATION OF NITROGEN IN NITRO, NITROSO AND AZO COMPOUNDS

MUHAMMAD ASHRAF

Department of Pharmacy, Panjab University, Lahore (Pakistan)

AND

M. K. BHATTY AND R. A. SHAH

West Regional Laboratories, P.C.S.I.R., Lahore (Pakistan)

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The determination of nitrogen in nitro, nitroso, and azo compounds by the direct application of Kjeldahl's method leads to low results, particularly when the content of nitrogen attached to oxygen exceeds 10%[1]. Many reagents have, therefore, been suggested for reduction of these types of nitrogen before the Kjeldahl digestion. The reduced nitrogen is then converted to ammonium sulphate from which ammonia is distilled and titrated.

It has been shown, however, that the distillation step in the Kjeldahl method can be eliminated advantageously. This can be achieved by employing either the formaldehyde reaction[2] or the determination of ammonia[3] with hypochlorite. Nitrogen has been determined by the latter method in organic compounds on the sub-micro[4], micro, semimicro[5] and macro scales and in agricultural and animal products[6].

Clearly, the possibility of determining nitrogen in nitro groups, etc., in organic compounds would make this method much more widely applicable. This required an investigation of the various reducing agents with a particular view to determining nitrogen eventually by the hypochlorite method. Some of the reductants successfully used in the usual Kjeldahl method are thiosalicylic acid[7], aromatic hydroxy compounds[8], phenol and zinc dust[9], zinc in methanol and hydrochloric acid[10], zinc alone[11], potassium persulphate and zinc dust[12], stannous chloride[13], sulphur[14], iron and aluminium[15]. Hydriodic acid[16] and various carbohydrates[17,18] have also been employed. Recent work in the field, particularly by BRADSTREET[18], indicates that sucrose brings about a quantitative reduction of oxygen-bound nitrogen in organic nitrogenous compounds.

We have shown that either glucose or zinc in methanol and hydrochloric acid is quite effective as a reductant and provides no interference in the later procedure. Glucose is particularly effective for the quantitative reduction of nitro, nitroso or azo groups in a large number of compounds having different amounts of nitrogen.

EXPERIMENTAL

Reagents

All the reagents used were of analytical reagent grade.

Special apparatus: digestion and titration vessels

A 250-ml round-bottom flask with a B_{19} socket and a 15 cm long B_{19} cone were used for the semi-micro procedure; for micro determinations the volume of the flask was reduced to 100 ml. The flasks attached to their cones served for the reduction and digestion. On completion of the digestion, the cones were detached and the flasks were employed for the titration step.

MICRODETERMINATION OF NITROGEN
Procedure for reduction

(1) Reduction with glucose

Weigh about 4–6 mg of sample into the flask. Add 0.7 g of the catalyst (a mixture of 0.625 g of potassium sulphate with 0.075 g of mercuric sulphate), 0.2–0.3 g of glucose and 3 ml of concentrated sulphuric acid, followed by a few pieces of alundum to aid smooth boiling. Attach the cone to the flask and heat gently on the usual digestion rack for 30 min. Then heat at the boiling temperature of the acid for another 2 h to effect complete decomposition of the substance.

(2) Reduction with zinc

Weigh 4–6 mg of sample into the flask. Add 1 ml of glacial acetic acid and warm to dissolve the substance. Add 0.1 g of zinc dust followed by 1 ml of methanol down the wall of the flask to rinse down the zinc dust. Then add hydrochloric acid, a few drops at a time, boiling the solution for 2 min after each addition. Add a total of 2 ml of hydrochloric acid in this way.

Attach the cone and evaporate the bulk of the contents of the flask by boiling, on the digestion rack, in the presence of a few alundum pieces. Do not evaporate to dryness. Add 1.5 ml of concentrated sulphuric acid and continue boiling for 15 min to drive out most of the previously added reagents. Cool the flask and detach the cone. Add 0.7 g of the catalyst (a mixture of 0.625 g of potassium sulphate and 0.075 g of mercuric sulphate) and 1 ml of sulphuric acid. Then reattach the cone and digest for 2 h.

Procedure for the determination of nitrogen

Cool the digest and dilute it about four-fold with water, rinsing the cone with this water. Add 60% sodium hydroxide solution dropwise with occasional shaking of the solution until the appearance of a yellow precipitate of mercuric oxide. Cool the solution and neutralize completely by gradual addition of sodium bicarbonate. Add about 2 g of potassium bromide and shake the flask again until an almost clear solution is obtained.

Run in an excess of 0.02 N sodium hypochlorite solution until the solution turns pale yellow. After 5 min add a known excess of 0.01 N arsenious oxide solution. Then back-titrate the excess of arsenite with the hypochlorite solution using aqueous 0.05% tartrazine indicator. Carry out a blank determination in the same way.

SEMIMICRO-DETERMINATION OF NITROGEN

In the case of glucose reduction for the semimicro-determination, 30–50 mg of the sample were taken and 1 g of glucose, 2.8 g of the catalyst (2.5 g of potassium sulphate

and 0.3 g mercuric sulphate) and 10 ml of sulphuric acid were used. 0.05 N sodium hypochlorite and 0.02 N arsenious oxide solutions were employed for the titration.

Zinc – hydrochloric acid reduction on the semimicro scale was carried out according to FISH[10].

Calculation

$$1 \text{ ml } 0.02 \text{ } N \text{ NaOCl} \equiv 0.0934 \text{ mg } N_2$$

DISCUSSION

The results in Table I indicate an accurate determination of nitrogen in nitro, nitroso and azo compounds when the reduction of these groups is effected with glucose. The method employing glucose is easy, neat and less time-consuming. Since the distillation step has been eliminated, the time required is less than that of the usual Kjeldahl method[16].

The method employing zinc reduction is more lengthy and involved than the glucose reduction. It can be seen from Table II that reduction with zinc is as widely applicable as that with glucose.

TABLE I

RECOVERY OF NITROGEN BY GLUCOSE REDUCTION

No.	Compound	Required	Found		
1	o-Nitrobenzoic acid	8.19	8.19	8.21	8.30
2	α-Nitroso-β-naphthol	8.09	8.14	7.97	8.06
3	2,4-Dinitrophenol	15.22	15.0	14.89	14.91
4	Azobenzene	15.38	15.32	15.29	15.36
5	p-Nitrobenzoic acid	8.38	8.33	8.42	8.40
6	5-Nitrosalicylic acid	7.65	7.71	7.57	7.70
7	o-Nitrophenol	10.07	10.18	10.13	10.11
8	p-Nitrobenzaldehyde	9.27	9.21	9.30	9.22
9	p-Nitroaniline	20.29	20.14	20.14	20.18
10	3,5-Dinitrobenzoic acid	13.20	13.19	13.31	13.23
11	1,3-Dinitrobenzene	16.67	16.44	16.51	16.32

TABLE II

RECOVERY OF NITROGEN BY ZINC—HYDROCHLORIC ACID REDUCTION

No.	Compound	Required	Found		
1	α-Nitroso-β-Naphthol	8.09	8.20	8.15	8.11
2	o-Nitrophenol	10.07	10.23	10.06	10.00
3	1,3-Dinitrobenzene	16.67	16.55	16.60	16.65
4	Azobenzene	15.38	15.45	15.51	15.32
5	2,4-Dinitrophenol	15.22	15.26	15.34	15.14
6	p-Nitroaniline	20.29	20.15	20.31	20.27

Hydrazine type of nitrogen

For hydrazine sulphate, p-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine and picrolonic acid, reduction with glucose or zinc is ineffective. The results for these

compounds are shown in Table III. It is of interest to note that all these compounds contain more than 20% of nitrogen. Somewhat higher recoveries of nitrogen were obtained for hydrazine sulphate with glucose than with zinc–hydrochloric acid reduction.

TABLE III

RECOVERY OF NITROGEN FROM HYDRAZINE TYPE COMPOUNDS BY GLUCOSE OR ZINC–HYDROCHLORIC ACID REDUCTIONS

No.	Compound	Required	Found					
			Reduction with Zn–HCl			Reduction with glucose		
1	p-Nitrophenylhydrazine	27.43	23.35	23.44	23.60	23.10	23.17	23.11
2	2,4-Dinitrophenylhydrazine	28.27	26.91	26.78	26.83	26.00	26.02	26.21
3	Picrolonic acid	21.20	16.32	16.11	16.21	14.70	14.41	14.55
4	Hydrazine sulphate	21.54	10.00	11.51	10.11	15.20	15.46	14.41

Attempts were made to improve the results for hydrazine type compounds by modifying the reduction. Aromatic aldehydes condense with hydrazine or its salts to form water-insoluble colourless aldazines[19]. It was considered that condensation of an aldehyde with hydrazines would make subsequent reduction more quantitative. An excess of salicylaldehyde in alcohol was, therefore, used for the formation of aldazines from the hydrazine compounds. The resultant products were digested as such with sulphuric acid. No notable improvement was observed in the recovery of nitrogen. The condensation products were further reduced with glucose but again without success. The recovery of nitrogen did not exceed 85% .

SUMMARY

A method is described for the determination of nitrogen in nitro, nitroso and azo compounds by a Kjeldahl method without distillation. The compound is reduced with glucose or zinc in methanol and hydrochloric acid. The ammonium sulphate produced after the usual digestion is determined by hypochlorite–arsenite titration. A single vessel is used for reduction, digestion and titration.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'azote dans des nitro-, nitroso- et azocomposés au moyen d'une méthode de Kjeldahl sans distillation. La substance est réduite au moyen de glucose ou de zinc en milieu méthanol–acide chlorhydrique; le sulfate d'ammonium formé est titré à l'aide d'hypochlorite et d'arsénite.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung des Stickstoffs in Nitro- Nitroso- und Azoverbindungen nach Kjeldahl ohne Destillation. Die Substanz wird mit Glucose oder Zink in methanolhaltiger Salzsäure reduziert und das gebildete Ammoniumsulfat durch Hypochlorit - Arsenit Titration bestimmt. Die Methode versagt bei Hydrazinen und Pikrolonsäure.

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CATION-EXCHANGE BEHAVIOR OF CALCIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

SANTOSH K. MAJUMDAR* AND ANIL K. DE

Department of Chemistry, Jadavpur University, Calcutta (India)

Systematic studies of the behavior of the alkaline earth metals, barium and strontium, in ion exchange methods have been carried out in this laboratory[1,2]; we have now extended this work to cover calcium.

SCHUBERT *et al.*[3] separated trace amount of beryllium from calcium on Dowex-50 with sulphosalicylic acid ($0.02\ M - 0.1\ M$) at pH 3.5–4.5 by selective elution. DAVIS[4] separated calcium from strontium on Zeokarb-225 at pH 4.25 in presence of EDTA (disodium salt) when all the strontium is retained in the column. MORACHIVISKI AND GORDEEVA[5] separated molybdenum from calcium on anion exchanger PE′-9 (in the nitrate or chloride form) when only calcium passed through. Similarly aluminium is separated from calcium on Dowex 2 anion exchange resin in the citrate form[6].

Further cation exchange studies of calcium have not previously been reported. This paper describes systematic studies on the cation exchange behavior of calcium on Dowex 50W-X8 (hydrogen form) following the same pattern as in case of barium and strontium[1,2]. Calcium has been separated from barium(II), copper(II), zinc, cadmium, mercury, and iron(III).

* Research Fellow, Council of Scientific and Industrial Research (India).

The apparatus was the same as before.

Calcium nitrate solution (about 5 mg/ml). About 17.7 g of calcium nitrate (Merck) was dissolved in 600 ml of water. The solution was standardised volumetrically by titration with permanganate after precipitation as oxalate. The cation exchange resin was Dowex 50W–X8 (Dow Chemical, Midland, Mich., U.S.A.), 50–100 mesh (hydrogen form). The resin was treated as before.

EXPERIMENTAL, RESULTS AND DISCUSSION

Ion exchange studies

An aliquot of solution containing 32.65 mg of calcium was used, the procedure being identical with that followed for strontium. The ion exchange behavior towards nitric acid and hydrochloric acid is shown in Fig. 1. Calcium can be quantitatively recovered by elution with 200 ml of nitric acid (2–4 M), hydrochloric acid (2–4 M), ammonium chloride (2–4 M), sodium nitrate (2–3 M) and ammonium acetate (1–4 M). When the elution peak was observed in a 50-ml fraction other than the first, the particular fraction was further collected in two 25-ml portions to determine the exact position of the peak (e.g. with mineral acids). The eluting agents can be arranged in order of increasing efficiency: citric acid < sodium nitrate = ammonium chloride < hydrochloric acid = ammonium acetate = nitric acid. Acetic acid–ammonium acetate mixtures were not satisfactory (No. 6, Table I). The effluent fractions were determined
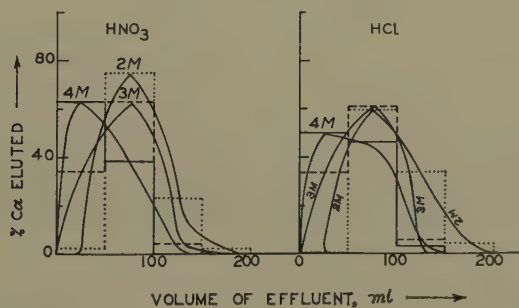
Fig. 1. Cation-exchange behavior of calcium with HCl and HNO₃ as eluants.

trimetrically with permanganate. In the case of strong acid eluants, the fractions were evaporated to dryness, then dissolved in water and used directly for analysis. Calcium was directly precipitated as oxalate when sodium nitrate and ammonium chloride or acetate were used as eluting agents.

Ion exchange separations

Separation from copper, zinc, cadmium, mercury and iron(III). KEMBER et al.[8] studied several organic eluants such as n-pentyl alcohol, n-propyl alcohol, methyl alcohol, ethyl methyl ketone and acetone. Copper was separated from iron by selective elution with ethyl methyl ketone containing 9% of 1.5 N hydrochloric acid. Similarly, copper was separated from nickel with acetone containing 4% hydrochloric acid and 5% water on Zeokarb-225, nickel being retained.

TABLE I

BEHAVIOR OF CALCIUM TOWARDS VARIOUS ELUTING AGENTS

Calcium = 32.65 mg; weight of oven-dried resin = 12.612 g

No.	Eluting agent	Calcium recovery % (50-ml fraction of effluent)				Total calcium recovery %	Elution constant E	Bed distribution coefficient D = r/E
		I	II	III	IV			
1	HNO₃, 1 M	—	—	—	6.66	6.66	—	—
	1.5 M	—	8.78	56.92	29.06	94.76	0.2892	3.538
	2 M	1.82	75.04	22.71	1.51	101.08	0.3812	2.623
	3 M	34.5	62.96	4.54	—	102	0.5585	1.791
	4 M	63.11	39.34	—	—	102.45	1.044	0.958
2	HCl, 1 M	—	—	3.02	16.65	19.67	—	—
	1.5 M	—	31.78	56.91	6.96	95.65	—	—
	2 M	0.9	59.02	34.5	3.93	98.35	0.3812	2.623
	3 M	33.59	60.53	5.45	1.2	100.77	0.5585	1.791
	4 M	50.24	46.91	3.93	—	101.08	1.044	0.958
3	NH₄Cl, 1 M	—	—	1.5	16.81	18.31	—	—
	2 M	—	59.43	36.01	3.9	99.34	0.3812	2.623
	3 M	19.51	73.21	6.3	—	99.02	0.3812	2.623
	4 M	36.32	58.83	3.6	—	98.75	0.3812	2.623
4	NaNO₃, 1 M	—	—	5.7	30.01	35.71	—	—
	2 M	—	68.42	28.81	2.4	99.63	0.3812	2.623
	3 M	24.01	64.52	11.4	—	99.93	0.3812	2.623
5	CH₃COONH₄, 0.5 M 1 M	—	27.31	57.03	14.51	98.85	0.3812	2.623
	2 M	42.02	53.42	3.6	—	99.04	0.3812	2.623
	4 M	53.42	39.01	9.01	—	101.44	1.044	0.958
6	CH₃COOH + CH₃COONH₄ pH = 4.2	—	—	16.81	36.6	53.41	—	—
7	Citric acid (5%) pH = 5.8	—	—	18.43	44.25	62.68	—	—

<div align="center">

TABLE II

ION-EXCHANGE SEPARATIONS OF CALCIUM

</div>

No.	Foreign ion	Added mg	Calcium found mg	Recovery %
I	Cu(II)	21.6	33.12	101.4
2	Zn(II)	20	33.51	102.6
3	Cd(II)	20	34.17	104.1
4	Hg(II)	20	33.6	102.9
5	Fe(III)	20.7	32.54	99.63

<div align="center">

(Ca = 32.65 mg)

</div>

Calcium can be separated from copper(II), zinc(II), cadmium(II), mercury(II) and iron(III) with 400 ml of 80% acetone which is 1 N in hydrochloric acid (Table II). This mixture elutes all these ions but not calcium, which is afterwards eluted with 200 ml of 2 M hydrochloric acid. The above mixture partly elutes cobalt(II) (about 50%) and manganese(II) (up to 8%) so that separations from calcium are not quantitative. Similar attempts to separate calcium from nickel and magnesium were not successful, since these metals were not eluted.

Separation of calcium, strontium and barium. Calcium can be quantitatively eluted with 200 ml of 1 M ammonium acetate which fails to elute barium; this provides an easy method of separation, for barium can later be eluted with 200 ml of 4 M ammonium acetate. The effluents were collected in 25-ml fractions, calcium being determined as before, and barium iodometrically. Fig. 2 illustrates the calcium–barium separations obtained. Calcium (9.3 mg) has been separated from as much as 10 times the amount of barium.

The ion-exchange characteristics of strontium and barium on a Dowex 50 column have already been studied. It is interesting to compare the separation factors for barium–calcium and barium–strontium on the basis of their bed distribution co-efficients under comparable conditions. The common eluting agents, nitric acid (2–9 M), sodium nitrate (2 M) and ammonium acetate (4 M) were used for these calcula-
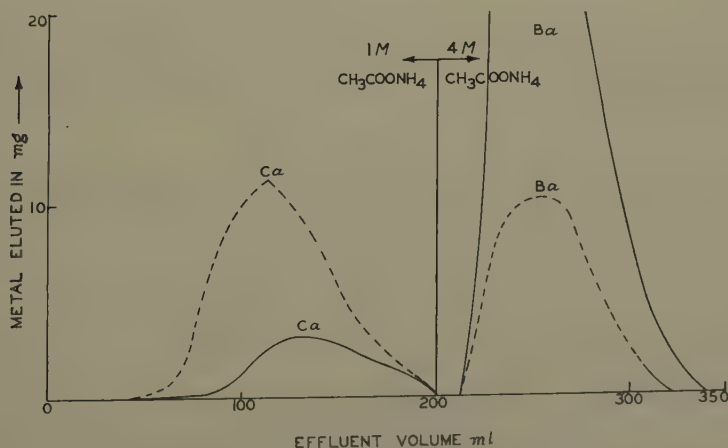
Fig. 2. Separation of barium from calcium.

tions. Table III shows that the best separation of barium from calcium is obtained with 1 M ammonium acetate, since the separation factor is large. Under the same conditions the separation of calcium from strontium is not quantitative; nearly 10%

TABLE III

SEPARATION FACTORS OF BARIUM–CALCIUM AND BARIUM–STRONTIUM

Eluant	Bed distribution coefficient			Separation factor D_{Ba}/D_{Ca}	Separation factor D_{Ba}/D_{Sr}
	Barium	Strontium	Calcium		
HNO_3, 2 M	2.683	3.846	2.623	1.023	0.6996
HNO_3, 3 M	1.872	1.136	1.791	1.045	1.647
HNO_3, 4 M	1.06	1.136	0.958	1.107	0.933
$NaNO_3$, 2 M	4.306	2.941	2.623	1.604	1.657
CH_3COONH_4, 1 M	very large	large	2.623	large	small
CH_3COONH_4, 4 M	2.683	1.136	0.958	2.801	2.361

of the strontium accompanies the calcium. This is evident from their D-values and has been confirmed experimentally.

The net operations in this method take 5–6 h. The results are reproducible to ±3%.

SUMMARY

The cation-exchange behavior of calcium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid are examined as eluants. Calcium can be separated from copper(II), zinc(II), cadmium(II), mercury(II), iron(III) and from barium. Separation factors for barium–calcium and barium–strontium are evaluated.

RÉSUMÉ

Les auteurs ont examiné le comportement du calcium sur échangeur de cations (Dowex 50W-X8), permettant une séparation d'avec Cu, Zn, Cd, Hg(II), Fe(III) et Ba. Des facteurs de séparation Ba–Ca et Ba–Sr sont donnés.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten des Ca bei der Trennung von Cu, Zn, Cd, Hg-(II), Fe-(III) und Ba mit dem Austauscherharz Dowex 50W-X8. Die Trennungskoeffizienten für Ba–Ca und Ba–Sr werden angegeben.

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CONTINUOUS FLOW MONITOR FOR SCANNING ³²P-CONTAINING EFFLUENTS FROM CHROMATOGRAPHY COLUMNS*

A. R. KRALL** AND L. P. ZILL

Photosynthesis Group, Research Institute for Advanced Studies, Baltimore, Md. (U.S.A.)

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he chromatography of ³²P-labeled materials is highly facilitated by continuous etection of radioactivity in the effluent. Owing to the highly energetic β-ray emission ³²P, sensitivity of detection presents no problem and it is therefore possible to do is by a variety of systems. However, certain disadvantages are associated with ese systems. Among these are difficulty of decontamination, necessity of special, stly GM tubes and large hold-up volumes.

In our work we have been separating ³²P-labeled phosphate esters by ion exchange romatography and ³²P-labeled phospholipids by silicic acid chromatography. For is work we have developed an extremely simple and flexible system for monitoring e effluent for radioactivity which is free of the disadvantages mentioned above. It the purpose of this paper to describe this method.

CONSTRUCTION

he heart of this system consists of a spiral of plastic capillary tubing positioned just er the mica window of an end-window GM tube. Clay–Adams Intramedic poly-hylene tubing serves admirably for this purpose. This tubing is available in a number sizes ranging between 0.28 and 2.92 mm internal diameter. We have routinely used e size having an internal diameter of slightly over 1 mm. Fig. 1 is a photograph picting one type of spiral arrangement. The column effluent is led into the tubing means of either a small standard taper or ball and socket glass joint. The joint drawn down to a size sufficient to give a tight slide fit into the plastic tubing. romatographic columns of the type described by HIRSCH AND AHRENS[1] possess a all ground glass joint which will accept a hypodermic needle. In this case it is ssible to insert the proper gauge needle directly into the tubing.

Depending on the availability of shop facilities, a considerable number of arrange-ents are possible. Our arrangement is that shown in Fig. 1. A cross-sectional diagram this apparatus is depicted in Fig. 2. The spiral is wound on a set of prongs mounted a machined brass cylinder. The brass cylinder is equipped with a rod for mounting th a standard laboratory clamp. The bottom of this cylinder is so designed that it

makes a slide fit with another machined brass cylinder containing the thin window GM tube mounted in its socket. The two cylinders are held together by spring detents attached to the lower cylinder. These detents seat in a groove as shown in Fig. 2. Intermittent monitoring of the effluent from a number of columns can be accomplished by equipping each with a spiral and shifting a single counting tube from one to another as desired.

Fig. 1. Photograph of flow monitor, disassembled to show both the GM tube holder and the spiral arrangement.

Since the detector system is ordinarily located in close proximity to the chromatographic column containing the radioactivity, adequate shielding must be provided. The apparatus depicted in Fig. 1 possesses adequate shielding, because of the brass case, except for the end-window itself. Extraneous radiation at this point is excluded by inverting a heavy glass caster cup over the spiral. It is obvious that manifold varieties of lead shielding may also be employed.

In the particular case shown in Fig. 1, the spiral exposed to the counting tube contains 0.8 ml sample volume. The ^{32}P in the liquid is counted with approximately 6.2% counting efficiency, essentially the same efficiency with which it would be

...unted if plated out on a planchet and counted with the same GM tube. Relative
...nsitivity of detection is apparent from a doubling of the count rate above a 40
...ounts/min background level when $5 \cdot 10^{-4} \mu C$ of ^{32}P is present in the spiral.

Since absolutely constant flow rates would be essential for the calibration of this
...stem in terms of the actual radioactivity present we have made no attempt to use
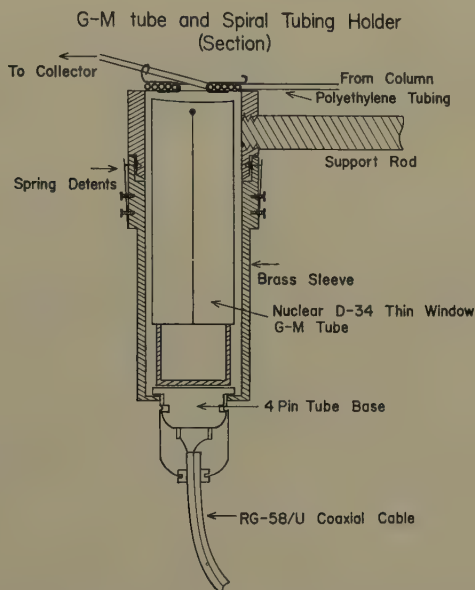
Fig. 2. Cross sectional diagram of flow monitor showing details of construction.
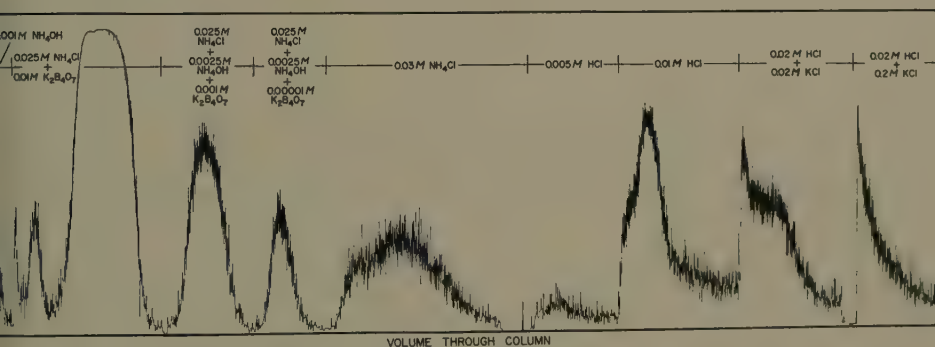
g. 3. Separation of ^{32}P-labeled compounds from Wintex barley by the method of KHYM AND
COHN[3].

for this purpose. Instead, when it was deemed necessary to obtain quantitative
...ta for radioactivity in the column effluents, we have resorted to ancillary methods
...ch as dipping-tube counting or the plating out of representative samples for end-
...indow counting.

Chromatographic procedures involving the use of organic solvents, such as the separation of phospholipids[1,2], introduce a possible source of contamination when used with the above described system. This is represented by the leaching out of plasticisers, usually phthalate esters, from the plastic tubing by the organic solvents used as eluents. This situation is circumvented by the use of Teflon tubing. Such tubing, in several sizes, is used as insulation in electronic equipment and is available from electronic supply houses.

Fig. 3 presents a typical application of the system described in this paper. It represents the separation of ^{32}P-labeled phosphates in a plant extract by the ion exchange system of KHYM AND COHN[3]. Direct monitoring of the effluent permits the collection of several large fractions as dictated by the record of radioactivity appearing on the chart.

Although we have studied the identification of the various materials represented by the peaks in Fig. 3, it is not our purpose to discuss them here. The tracing was obtained by recording the output of a Berkeley count ratemeter on a Weston recorder.

It is unfortunately true that the described system cannot be used for the detection of low-energy β-rays. Such systems have been described[4,5] but are of considerably greater complexity since they must meet much greater sensitivity demands.

SUMMARY

A continuous flow monitor for scanning ^{32}P-containing effluents from chromatography columns is described. The separation of ^{32}P-labeled compounds from barley is presented as an illustration of the results obtained with the system.

RÉSUMÉ

Une méthode est proposée permettant, lors de la chromatographie de substances avec phosphore marqué, une détection continue de la radioactivité de l'effluent.

ZUSAMMENFASSUNG

Beschreibung eines Gerätes, das den Gehalt an ^{32}P in einem ^{32}P enthaltenden Effluat einer chromatographischen Kolonne kontinuierlich anzeigt.

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RINGOFEN–TÜPFELKOLORIMETRISCHER NACHWEIS CARBAMATBILDENDER METALLIONEN NEBEN ALUMINIUM UND ANDEREN METALLEN. I

H. MALISSA UND L. J. OTTENDORFER

Institut für analytische Chemie der Technischen Hochschule, Wien (Österreich)

Eine grosse Anzahl analytischer Bestimmungen beruht darauf, dass die aus wässriger Lösung gefällten Metalldithiocarbamate in ein mit Wasser nicht mischbares organisches Lösungsmittel extrahiert und dann bestimmt werden.

ŠEDIVEC UND FLEK[1] haben die Löslichkeit einiger Metalldithiocarbamate in einer Reihe von Solventien bestimmt und festgestellt, dass neben Chloroform besonders Pyridin als Lösungsmittel hervorragend geeignet ist. Da aber Pyridin mit Wasser mischbar ist, ergibt sich die Möglichkeit, einen Metalldithiocarbamatniederschlag in Form eines Tüpfelflecks auf Filterpapier auf dem noch feuchten Papier zum Ring zu waschen, was mit Rücksicht auf die Zersetzlichkeit der Niederschläge sehr erwünscht ist.

Wird nun ein Tüpfelfleck, der neben einem mit Na-DDTC fällbaren eine beliebige Menge eines nicht fällbaren Ions enthält, mit einer Na-DDTC-Lösung besprüht, die nötigenfalls auch Puffersubstanzen und Hilfskomplexbildner enthalten kann, so entsteht sofort ein Niederschlag von Metalldithiocarbamat. Das nicht gefällte Ion kann durch Waschen[2] entfernt und das Metalldithiocarbamat mit Pyridin zum Ring gewaschen werden.

Eine auf diese Weise durchführbare Trennung soll am Beispiel Al–Cu erläutert werden: Ein Tropfen einer Lösung, die neben Cu^{+2} eine beliebige Menge Al^{+3} enthalten darf, wird mit einer Kapillarpipette auf ein Rundfilter Sch & Sch 589², 5.5 cm, aufgebracht und mit der Reagenslösung besprüht, die 2% Natriumdiäthyldithiocarbamat, 5% Weinsäure und soviel Ammoniak enthält, dass der pH-Wert zwischen 8 und 9 liegt. Während das Cu^{+2} sofort als Dithiocarbamat gefällt wird, bleibt Al^{+3} als Tartratkomplex in Lösung und wird durch Waschen entfernt. Durch Abpressen mit Filterpapier wird die Hauptmenge der Flüssigkeit entfernt, das Filter auf den Ringofen gelegt und das Kupferdithiocarbamat mit Pyridin in bekannter Weise zum Ring gewaschen[2]. Die grünlich-braune Eigenfarbe des Kupferdithiocarbamatniederschlages kann bereits zum semiquantitativen Nachweis für Kupfer verwendet werden[2]. In Gegenwart anderer, mit Dithiocarbamat fällbarer Ionen, besonders wenn diese gefärbte Niederschläge bilden, muss das Kupfer durch geeignete Trennungsoperationen von störenden Beimengungen befreit werden. Zu diesem Zweck muss die ausserordentlich wirksame Maskierung, die durch die hohe Stabilität der Metalldithiocarbamate bewirkt wird, durch Zerstörung des Dithiocarbamates beseitigt werden.

Am besten geschieht dies durch Räuchern des leicht angefeuchteten Filters über Brom und Ammoniak. Der Überschuss des Oxydationsmittels wird durch kurzes Erwärmen im Trockenschrank oder unter der Trockenlampe unschädlich gemacht. Die Art der weiteren Fällungs- und Auswaschoperation richtet sich nach den zu erwartenden Beimengungen, worüber in Kürze berichtet werden wird. Auf die geschilderte Weise kann nicht nur Kupfer, sondern jedes andere mit Dithiocarbamat fällbare Ion neben beliebigen Mengen eines nicht mitfallenden Ions, wie z.B. Aluminium, nachgewiesen werden. Die Erfassungsgrenze der Bestimmung ist lediglich durch die Mindestmenge gegeben, die mit der gewählten Nachweisreaktion im Ring erfasst werden kann. Selbstverständlich kann durch mehrmaliges wechselweises Auftüpfeln von Probe und Reagens eine Anreicherung des gesuchten Ions erreicht werden.

ZUSAMMENFASSUNG

Kleine Mengen gewisser Kationen werden durch Na-DDTC in Gegenwart beliebiger Mengen nicht mitfallender Kationen im Tüpfelfleck gefällt und die anderen durch Waschen entfernt. Me-DDTC wird *ohne* vorherige Trocknung mit Pyridin zum Ring gewaschen und das Kation dort — gegebenenfalls nach Entfernung störender Begleiter — nachgewiesen. Die Methode wird am Beispiel Al–Cu erläutert.

SUMMARY

Small amounts of cations yielding insoluble dithiocarbamates are fixed on filter paper by precipitation with Na-DDTC. Other cations are removed by washing. On the Weisz-Ring oven, the metal-DDTC is moved to the ring by washing with pyridine *without* prior drying. Identification is carried out in the ring zone, if necessary after destruction of carbamate and removal of interfering cations. Cu – Al is given as example.

RÉSUMÉ

Une méthode à la touche, sur papier filtre, est proposée pour l'identification et le dosage semi-quantitatif de certains cations. La séparation cuivre–aluminium est donnée comme exemple.

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SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF URANIUM WITH SOLOCHROMATE FAST RED

J. KORKISCH AND G. E. JANAUER

Analytical Institute, University of Vienna (Austria)

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INTRODUCTION

Only a few methods have up till now been reported for the application of azo dyes to the spectrophotometric determination of uranium. CHENG[1], and GILL et al.[2] have described a very sensitive method for the determination of trace amounts of uranium employing the azo dye, 1-(2-pyridylazo)-2-naphthol (PAN), while POLLARD et al.[3] proposed 4-(2-pyridylazo)-resorcinol as a possible analytical reagent for the colorimetric estimation of cobalt, lead and uranium.

FOREMAN et al.[4] showed that the arseno azo dye thorin (sodium salt of 1-(o-arsenophenylazo)-2-naphthol-3,6-disulphonic acid, thoron, thoronol) can be applied for the spectrophotometric determination of microgram amounts of uranium(IV). Recently a similar dye, neothorin (3-(2-arsenophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid; arsenazo) has been introduced as a photometric reagent for the determination of uranium(VI) by FRITZ AND JOHNSON-RICHARD[5] and others[6-8].

Research work in this laboratory showed that among the azo dyes examined, Solochromate Fast Red 3G 200 (C.I. Mordant Red 19; 6-amino-4-chloro-1-phenol-2-sulfonic acid → 3-methyl-1-phenyl-5-pyrazolone) can be employed as a sensitive and relatively specific reagent for the determination of uranium(VI). Owing to the low solubility of this dyestuff in water a number of organic solvents were investigated for their suitability as a medium for the spectrophotometric determination of uranium. The best results were obtained in methanolic medium in which also the solubility of inorganic salts is sufficiently high. By the addition of EDTA it was possible to eliminate interference by small amounts of copper, iron and thorium. Interfering ions which cannot be masked by means of EDTA must be separated from uranium before the final determination with Solochromate Fast Red can be carried out. For the purpose of uranium separation, ion exchange methods have been developed in this laboratory which ensure quantitative removal of the interfering ions[9-14]. Among these methods the separation of uranium from practically all elements by means of column operations in hydrochloric acid–ethanol[13] or –methanol[14] solutions employing the strongly basic anion exchanger Dowex 1 proved to be most suitable.

SOLUTIONS AND REAGENTS

Uranium standard solutions

An exactly weighed amount of reagent grade uranyl nitrate was quantitatively converted to uranyl chloride by repeated evaporation with 6 N hydrochloric acid.

The uranyl chloride obtained was dissolved in $1 N$ hydrochloric acid. This uranium stock solution contained a gravimetrically[15] and volumetrically[16] determined amount of 1 mg uranium/ml of $1 N$ hydrochloric acid. By dilution with $1 N$ hydrochloric acid, standard solutions of lower uranium concentrations were prepared.

Dyestuff solutions

500 mg of Solochromate Fast Red 3G 200 (this dyestuff was kindly furnished by the Imperial Chemical Industries, Hexagon House, Blackley, Manchester, England) of the following formula:
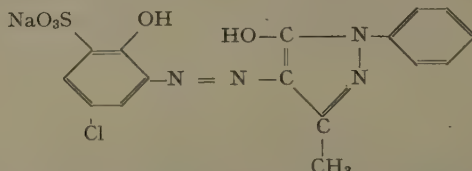
were dissolved in 100 ml of pure methanol. Since this dyestuff was accompanied by a small amount of inorganic substances insoluble in methanol, it was filtered after digestion for 6 h. This solution will further be referred to as 0.5%. By dilution with methanol 0.25% and 0.1% solutions of the dyestuff were prepared.

Standard solutions of other ions

Many solutions of common foreign cations and a number of anions in $1 N$ hydrochloric acid were applied.

Organic solvents

The following solvents, all chemically pure, were employed: methanol, ethanol, n-propanol, isopropanol, acetone, ethylene glycol and dioxane.

APPARATUS

The absorbance measurements were carried out in 1-cm cells using a Beckman spectrophotometer model B. For the preparation of the measuring solutions 10-ml flasks or 25-ml beakers were employed.

CHOICE OF SUITABLE WAVELENGTH

To 1 ml of a uranium standard solution containing 100 μg of uranium, 1 ml of the 0.5% dyestuff solution and 1 ml of 2.5 M sodium acetate solution were added. This solution was diluted to the mark with methanol and measured against a reagent blank in the wavelength range from 450 to 550 mμ. The results of these measurements are recorded in Fig. 1 from which it is seen that the maximum absorbance of the uranium dyestuff complex is found at 490 mμ.

INFLUENCE OF ACIDITY

Since no complex formation occurs in hydrochloric acid media, increasing amounts of 2.5 M sodium acetate solution were employed. The solutions contained 100 μg of uranium dissolved in 1 ml of 1 N hydrochloric acid, 1 ml of the 0.5% dyestuff solution and 0–3.0 ml of the sodium acetate solution. These solutions were diluted to the mark with methanol and measured against reagent blank solutions at 490 mμ. These

measurements showed (see Fig. 2) that after a steep increase of absorbance when 0.4–1.0 ml of the sodium acetate solution was present, further addition of sodium acetate had no effect on the absorbance up to an amount of 2.5 ml, whereafter a slight decrease could be noticed. For this reason 1 ml of the sodium acetate solution per 10 ml was applied in all further experiments.
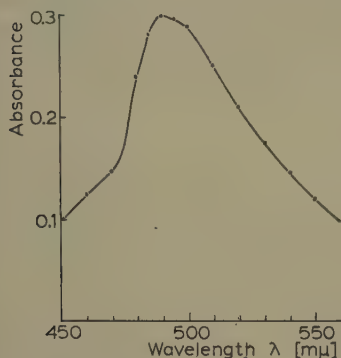
Fig. 1. Choice of suitable wavelength.
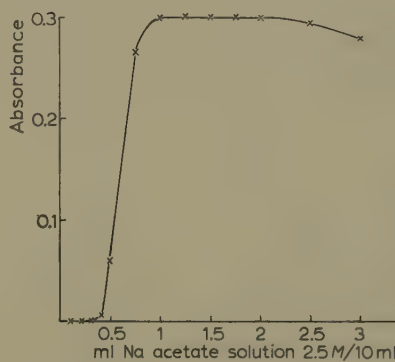
Fig. 2. Influence of acidity.

INFLUENCE OF DYESTUFF CONCENTRATION

The solutions contained 100 μg of uranium dissolved in 1 ml of 1 N hydrochloric acid, 2.5–8.0 ml of the 0.1% dyestuff solution and 1 ml of 2.5 M sodium acetate solution. These solutions were diluted to the mark with methanol and measured against reagent blank solutions at 490 mμ. Variations in the dyestuff concentration from 2.5–7.5 ml/10 ml of measuring solution did not change the maximum absorption whereas at lower concentrations the absorbance increased to a maximum in presence of 2.5 ml of the dyestuff solution (see Fig. 3). Consequently 1 ml of a 0.5% dyestuff solution corresponding to 5 ml of the 0.1% solution was used for further work.

INFLUENCE OF SOLVENTS

Solutions containing 100 μg of uranium in 1 ml of 1 N hydrochloric acid, 1 ml of the 0.5% dyestuff solution and 1 ml of 2.5 M sodium acetate were diluted to the mark with the following solvents: methanol, ethanol, n-propanol, isopropanol, ethylene glycol, acetone and dioxane, and measured against corresponding reagent blank solutions at 490 mμ. The results (see Table I) showed that the highest absorbance was reached in methanol and acetone; but in the latter solvent no reproducible results could be obtained.

TABLE I
INFLUENCE OF SOLVENTS

Solvent	Absorbance at 490 mμ
methanol	0.300
ethanol	0.265
n-propanol	0.240
isopropanol	0.280
ethylene glycol	0.260
acetone	0.340
dioxane	0.290

When the organic solvent was replaced by varying amounts of water, it was found that with up to 4 ml of water per 10 ml of measuring solution no change of absorbance could be observed. At higher water concentrations the dyestuff was precipitated.

INFLUENCE OF TIME, TEMPERATURE AND SEQUENCE OF ADDITION

Experiments showed that the uranium dyestuff complex is of very high stability, the absorbance being constant for at least 24 h. In the range from 10–30° no effect of temperature on the absorbance was noticeable. The sequence of reagent addition should be performed as described in the working procedure.
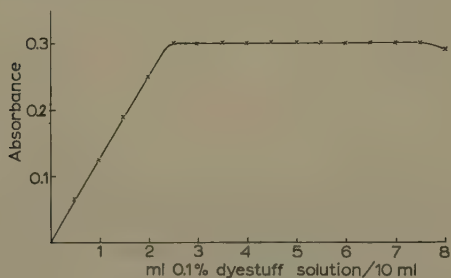
Fig. 3. Influence of dyestuff concentration.   Fig. 4. Calibration curves.
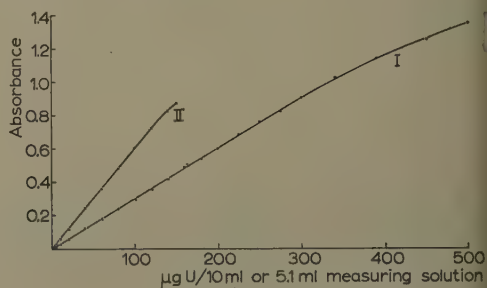
INFLUENCE OF FOREIGN IONS

In Table II the percentage error of uranium measurements in presence of numerous ions is recorded. All the solutions contained 100 μg of uranium and different amounts of the ions under investigation. They were prepared as described under (a) (see working procedure): 1 ml of a uranium standard solution containing 100 μg of uranium and a certain volume of a standard solution of the ion in question were evaporated to dryness on the water bath, etc.

It can be seen that some elements interfere more or less seriously with the uranium determination. In order to remove these ions from uranium the anion exchange separation methods[9-14] mentioned before must be applied, thus making possible uranium determinations in a variety of materials, e.g. in marine sediments. Small amounts (up to 100 μg) of iron(III), copper(II) and thorium(IV) are masked by the EDTA present.

CALIBRATION CURVES

In 10 ml of measuring solution

The solutions contained 0–500 μg of uranium dissolved in 1 ml of 1 N hydrochloric acid, 0.1 ml of 0.1 M EDTA, 1 ml of 0.5% dyestuff solution and 1 ml of 2.5 M sodium acetate. These solutions were made up to volume with methanol and measured against a reagent blank solution at 490 mμ. From Fig. 4, curve I, it is seen that Beer's law holds from 0–300 μg of uranium.

In 5.1 ml of measuring solution

The solutions contained 0–150 μg of uranium dissolved in 0.5 ml of 1 N hydrochloric acid, 0.1 ml of 0.1 M EDTA, 1 ml of 0.25% dyestuff solution, 0.5 ml of 2.5 M sodium acetate and 3 ml of methanol. These solutions were then measured against a reagent

TABLE II

INFLUENCE OF FOREIGN IONS ON URANIUM DETERMINATION

Ion	Present as	Foreign ion (μg)	% error
Mg(II)	chloride	1000	+ 62.0
Ca(II)	chloride	1000	+ 56.0
Sr(II)	chloride	1000	— 1.0
Ba(II)	chloride	1000	+ 2.0
Al(III)	chloride	1000	+220.0
Sn(II)	chloride	1000	— 2.0
Pb(II)	chloride	1000	— 3.0
Bi(III)	chloride	1000	+ 19.0
Cu(II)	chloride	200	+ 16.0
Cu(II)	chloride	100	— 1.0
Zn(II)	chloride	1000	— 2.5
Cd(II)	chloride	1000	— 1.5
Hg(II)	chloride	1000	— 2.0
Y(III)	nitrate	1000	+108.5
La(III)	nitrate	1000	+ 12.0
Ce(III)	sulphate	1000	precipitation
Nd(III)	nitrate	1000	+106.0
Pr(III)	nitrate	1000	+112.4
Ti(IV)	chloride	1000	+200.0
Zr(IV)	chloride	1000	+ 80.0
Hf(IV)	chloride	1000	+ 11.7
Th(IV)	chloride	1000	+190.5
Th(IV)	chloride	100	+ 3.0
V(V)	vanadate	1000	+111.0
Cr(III)	sulphate	1000	+ 19.2
Mo(VI)	molybdate	1000	— 2.0
W(VI)	tungstate	100	+ 2.4
Mn(II)	chloride	1000	+ 1.0
Fe(III)	chloride	100	+ 1.0
Fe(III)	chloride	200	+ 15.0
Co(II)	chloride	1000	+ 0.8
Ni(II)	chloride	1000	+ 1.5
Pd(II)	chloride	1000	+280.0
Pt(IV)	chloride	1000	— 1.5
Br−	K-salt	2000	+ 25.0
I−	K-salt	2000	+ 2.5
F−	K-salt	2000	+ 11.0
NO_3^-	K-salt	2000	+ 3.0
SO_4^{-2}	K-salt	2000	— 25.0
$H_2PO_4^-$	K-salt	2000	— 2.5
CN−	Na-salt	2000	— 2.8
AsO_4^{-3}	Na-salt	2000	— 2.0
oxalate	Na-salt	2000	— 2.0
tartrate	K-salt	2000	+ 0.5
citrate[a]	K-salt	2000	— 1.0
SCN−	ammonium salt	2000	— 0.5

As the addition of citrate does not affect the uranium determination we tried to mask some seriously interfering ions by adding 0.1 ml of a 10% potassium citrate solution per 10 ml measuring solution. The following elements up to 1000 μg can effectively be masked: Th, La, Ce, Y, Nd and ... r. This fact however was not utilized for the development of the working procedure since all the ... ns recorded in Table II can easily be separated from uranium by means of anion exchange[9–14].

blank solution at 490 mμ. The results are recorded in Fig. 4, curve II, showing that Beer's law applies from 0–120 μg uranium.

<div align="center">WORKING PROCEDURE</div>

The uranium-containing solution e.g. an eluate after an ion exchange separation[9–14], is evaporated in a quartz dish to complete dryness and ignited to remove organic matter. The uranium oxide obtained is then taken up in 5–10 ml of 6 N hydrochloric acid and the solution evaporated to dryness on a water bath. The uranyl chloride is transferred quantitatively to a 25-ml beaker using a few ml of 1 N hydrochloric acid. This solution is then evaporated to complete dryness on the water bath. The residue is taken up as follows:

(a) in 1 ml of 1 N hydrochloric acid and left standing for 15 min with intermittent shaking of the beaker. Afterwards 0.1 ml of 0.01 M EDTA is added and the solution transferred to a 10-ml measuring flask, rinsing the beaker with altogether 6 ml of methanol. To this solution 1 ml of the 0.5% dyestuff solution and 1 ml of 2.5 M sodium acetate is added. After making up to volume with methanol, the solution is measured against a reagent blank solution at 490 mμ. By means of the calibration curve in Fig. 4, curve I, the amount of uranium in the measuring solution can be readily determined.

(b) in 1 ml of a mixture of 25 ml of 1 N hydrochloric acid and 25 ml of methanol and left standing for about 15 min with occasional shaking. Now 0.1 ml of the EDTA solution, 1 ml of 0.25% dyestuff solution, 0.5 ml of sodium acetate solution and 2.5 ml methanol are added. The mixture is homogenised by gently shaking the beaker and is then measured against a reagent blank solution at 490 mμ (the reagent blank solution must be prepared simultaneously). By means of the calibration curve II in Fig. 4 the amount of uranium contained in the measuring solution can readily be determined.

<div align="center">SENSITIVITY AND ACCURACY</div>

According to curves I and II in Fig. 4, amounts of 5 μg uranium/10 ml or 2.5 μg uranium/5.1 ml of measuring solution can still be determined. The percentage error in the concentration range from 10 to 300 μg of uranium/10 ml has an average value of $\pm$ 3%. Below 10 μg of uranium the error may increase to $\pm$ 5–10%. In 5.1 ml measuring solution the average percentage error is $\pm$ 4% except at concentrations below 5 μg uranium where it reaches a value of $\pm$8–12 %.

<div align="center">TABLE III</div>

<div align="center">DETERMINATION OF URANIUM IN MARINE MATERIALS</div>

Sample No.	p.p.m. uranium found by polarographic method	p.p.m. uranium found by Solochromate Fast Red-method
1	133	136
2	130	132
3	130	135
4	265	270
5	166	170
6	115	110
7	192	200
8	205	200
9	151	155

APPLICATION

n order to find out whether this method can also be applied to the uranium analysis
 marine materials *e.g.* manganese nodules, a number of samples were analysed.
fter separation and isolation of uranium by means of anion exchange[13,14], the ura-
um content of the eluates was determined both polarographically[13] and spectro-
hotometrically with Solochromate Fast Red. The results in Table III show that this
pectrophotometric determination is as reliable as the extensively used polarographic
ethod. The latter method is however superior when amounts of less than 1 μg
ranium/ml of measuring solution are present.

ACKNOWLEDGEMENTS

SUMMARY

method is described for the spectrophotometric determination of micro amounts of uranyl ions
th the azo dye, Solochromate Fast Red, which reacts with uranium(VI) in acetate-buffered
ethanol solution to form an orange-brown colored complex with maximum extinction at 490 mμ.
er's law is obeyed over a wide range of uranium concentrations. Only a limited number of
reign ions interfere, hence this method is generally applicable after removal of interfering ions
 anion exchange; *e.g.* uranium can be determined in marine materials.

RÉSUMÉ

e méthode est décrite pour le dosage spectrophotométrique de microquantités d'uranium(VI),
 moyen de rouge au chrome solide. En solution tampon, dans l'alcool méthylique il se forme
 complexe brun orange, avec extinction maximum à 490 mμ. Les ions génants sont éliminés au
éalable par échangeur d'ions.

ZUSAMMENFASSUNG

eschreibung einer spektrophotometrischen Methode zur Bestimmung von Mikromengen Uran
t Solochrom Fast Red, das mit Uran einen orangebraun gefärbten Komplex bildet. Störende
emdionen können mit einem Ionenaustauscherharz entfernt werden.

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SPECTROPHOTOMETRIC DETERMINATION OF IRIDIUM WITH STANNOUS IODIDE REAGENT

EUGENE W. BERG AND HUBERT L. YOUMANS

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La. (U.S.A.)

KEMBER AND WELLS[1] were able to detect 0.1 p.p.m. of iridium at 360 mμ by the stannous chloride method, but the intensity of color was found to vary considerably with time and temperature (little color developed at room temperature). No method of obtaining reproducible results adequate for colorimetric analysis was found. A serious difficulty was the very high absorbancy of the blank at 360 mμ. BERMAN AND McBRYDE[2] noted that hexachloroiridate solutions after boiling with hydrobromic acid produced a yellow solution upon the addition of stannous chloride in hydrochloric acid. The absorbancy maximum was at 485 mμ. If the stannous chloride were dissolved in hydrobromic acid, the maximum absorbancy shifted to 402 mμ and the solution was more stable and had a higher absorbancy. The data given indicate that the molar absorptivity is constant in the middle of the absorbancy *versus* concentration curve but decreases at both ends. When stannous bromide was used in place of stannous chloride, the sensitivity was increased by 10%, but the color was less stable.

The above results suggest that as the size of the halogen anion increases, the stannous halide reaction increases in sensitivity and stability. This coincides with the polarizability sequence of the halides of interest: I$^-$ > Br$^-$ > Cl$^-$. BERG AND YOUMANS[3] established this sensitivity order for the stannous halide reaction with rhodium(III). The stannous iodide reaction thus promised a more sensitive and stable analysis of iridium; the present work was undertaken to test that hypothesis.

EXPERIMENTAL

Apparatus and reagents

The spectra were recorded with a Beckman DK-1 spectrophotometer. Absorbancies at 446 mμ were measured with a Beckman DU spectrophotometer using 1-cm quartz cells.

Iridium(III) solutions were prepared by dissolving the trichloride in 0.3 N hydrochloric acid and standardizing by the method of GILCHRIST[4].

Tin(II) chloride solutions were prepared by dissolving 1 part by weight of SnCl$_2 \cdot$2H$_2$O in 1 part by volume of concentrated hydrochloric acid and diluting with 2 parts by volume of distilled water. For acidity calculations, this solution was considered to be 4 N in hydrochloric acid. Tin metal was placed in the stock solution.

All other reagents were of analytical grade and prepared as indicated.

commended procedure

Transfer the iridium solution to a 25-ml volumetric flask. Add sufficient hydro-
loric acid so that the final solution will be 1.3 N in HCl. Add 5 ml of 40% (w/v)
tassium iodide solution, mix, and heat for 10 min in a boiling water bath. Cool to
om temperature. Pipet 2 ml of the stannous chloride solution into the flask and
lute to volume with distilled water. Mix and heat the unstoppered flasks for 3 min
a boiling water bath. Cool immediately to room temperature in an ice bath. Measure
e absorbancy of the solution at 446 mμ *versus* a blank prepared identically to the
mple except for the omission of iridium. Determine the iridium concentration from
standard curve.

fect of temperature on solution absorbancy

The iridium is converted to the iodide complex by 10 min of heating with potassium
dide in the boiling water bath (Fig. 1). Upon the addition of tin(II) chloride solution
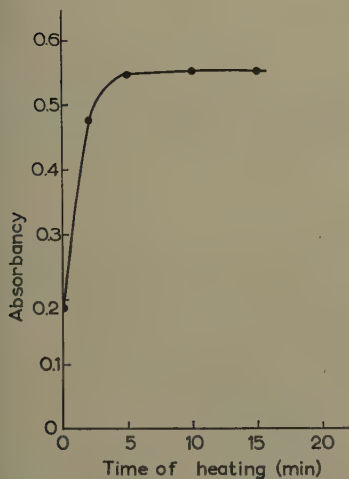
g. 1. Effect of time of heating on the con-
rsion of hexachloroiridite to hexaiodoiridite.
p.p.m. Ir used in the test solution. Absorb-
ancy measured at 446 mμ.
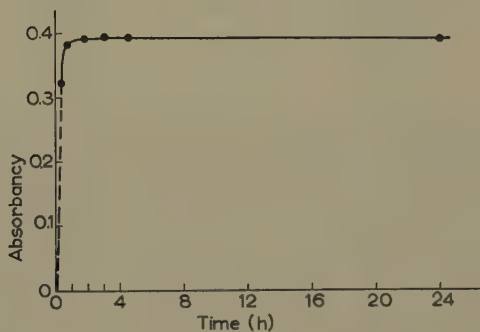
Fig. 2. Variation of solution absorbancy (446
mμ) with time of color development at room
temperature. 5.8 p.p.m. Ir used in the test solu-
tions.
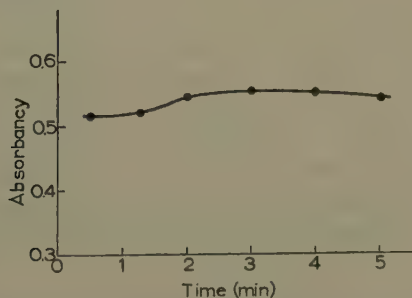
g. 3. Variation of solution absorbancy (446 mμ) with time of heating in boiling water bath after
e addition of stannous chloride solution and dilution to volume. 7.7 p.p.m. Ir used in the test
solutions.

to the hexaiodoiridite, a yellow to brown color develops that attains a maximum absorbancy after 2 h at room temperature (Fig. 2). The complex agrees in molar absorptivity and stability with the complex developed in the boiling water bath. The absorbancy of a solution heated in the water bath varies but little with heating periods of 1–5 min (Fig. 3). The maximum and most reproducible absorbancy is obtained with 3 min heating. Heating was chosen to speed the analyses. The absorbancy peak is at 446 mμ (Fig. 4) and the solution is stable for at least 24 h if kept in the dark.

Effect of hydrochloric acid concentration on solution absorbancy

The molar absorptivity of the iridium complex changes little as the hydrochloric acid concentration is changed from 1 to 2 N (Fig. 5). A precipitate of SnI$_2$ forms if the acid concentration is below 1 N; above 2 N, the molar absorptivity of the solution decreases slowly. A solution 1.3 N in hydrochloric acid was used in subsequent tests.
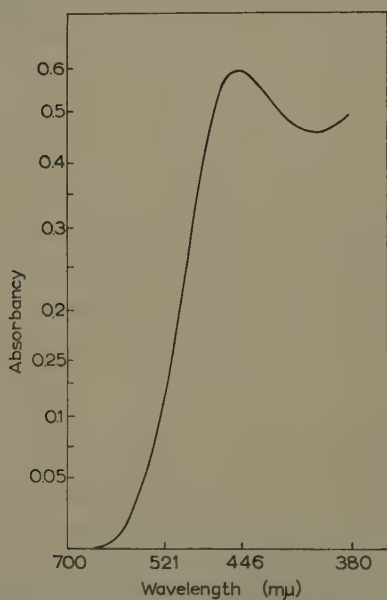
Fig. 4. Absorbancy curve of a stannous iodide iridium iodide solution containing 7 p.p.m. Ir.
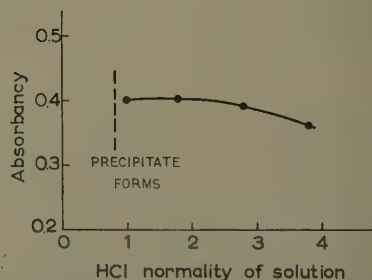
Fig. 5. Variation of solution absorbancy (446 mμ) with concentration of hydrochloric acid. 5.5 p.p.m. Ir used in test solutions.

Effect of potassium iodide concentration on solution absorbancy

The molar absorptivity initially increases rather rapidly with increasing iodide concentration (Fig. 6), but reaches a maximum before SnI$_2$ begins to precipitate.

Effect of stannous chloride concentration on solution absorbancy

Solution absorbancies increase only slightly with increasing stannous chloride concentration (Fig. 7). The absorbancies, however, were more reproducible if only 2 ml reagent was used.

Effect of diverse ions, salts, and sulfuric acid on solution absorbancy

The more common interferences and indications of the extent of their interference

e given in Table I. As in all of the stannous halide methods, a separation of iridium
om the platinum and other transition metals is necessary. During the reaction
riod, a small amount of iodine is formed. The table shows that this should not in-
ence the analyses.
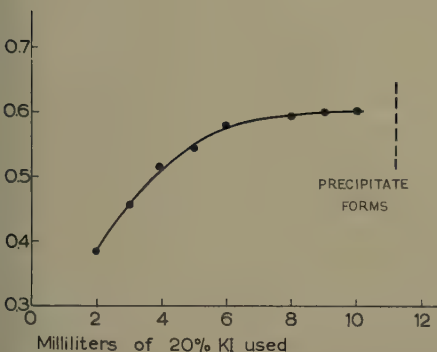
g. 6. Effect of amount of KI used on solution
sorbancy. 7.7 p.p.m. Ir used in the test
tions. Absorbancy measured at 446 mμ.

Fig. 7. Effect of amount of SnCl₂ used on solu-
tion absorbancy. 5.5 p.p.m. Ir used in the test
solutions. Absorbancy measured at 446 mμ.

TABLE I

E CONCENTRATION OF INTERFERENCES NECESSARY TO GIVE A 1% VARIATION IN SAMPLE ABSORB-
ANCY FOR A SAMPLE SOLUTION CONTAINING 4.8 p.p.m. IRIDIUM(III)

Interference	Concentration (p.p.m.)	Direction of change
Rh as RhCl₃	0.02	+
Pt as PtCl₂	0.09	+
Pd as PdCl₂	—	precipitates
Sn as SnCl₄	70	+
Co as CoCl₂	13	+
Fe as FeCl₃	13	+
Sb as SbCl₃	0.2	+
Ni as NiCl₂	46	+
Cu as CuCl₂	23	+
Ti as TiCl₄	4	—
Na₂SO₄	$4.0 \cdot 10^4$	—
NaCl	$1.2 \cdot 10^4$	+
I₂	1800	+
Cr as CrCl₃	27	+
H₂SO₄	$4.9 \cdot 10^3$	—

timum working range

The Ringbom plot (Fig. 8) shows the working range to be from 0.8 to 11.7 p.p.m.
lium. The system does not obey Beer's law, but is reproducible.

Precision of method

Six samples containing 4.9 p.p.m. iridium(III) showed an average deviation of 0.9% and a standard deviation of 1.1%. Another group of six samples containing 6.4 p.p.m. iridium(III) showed an average deviation of 0.9% and a standard deviation of 1.2%.
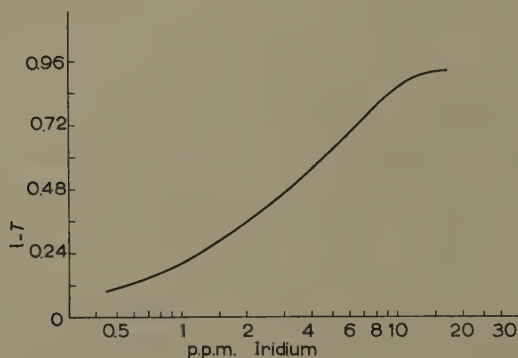
Fig. 8. Ringbom plot of iridium–tin(II) iodide complex determined at 446 mμ.

DISCUSSION

The need of a simultaneous method of analysis for rhodium and iridium led to the study of the stannous halide reactions. BERMAN AND MCBRYDE[2] failed to simultaneously determine these ions with stannous bromide reagent due to the instability of the rhodium complex. BERMAN AND IRONSIDES[5] subsequently stabilized the rhodium complex with perchloric acid but reported no work on the simultaneous analysis of rhodium and iridium. An effort was made in the present authors' laboratory to combine and modify the above papers into a simultaneous analysis for rhodium and iridium. The resulting molar absorptivity for the iridium complex was constant over a wider range than that of the unmodified procedure. Both iridium and rhodium singly yielded complexes with molar absorptivities sufficiently stable for our purpose, but in combined solutions the absorbancies were poorly reproducible and accurate only half of the time. Extreme variations often were observed. The perchloric acid that stabilized the rhodium complex made the iridium complex less stable and reproducible, but this did not account for the non-reproducibility of mixed solutions.

The stannous iodide method proved impractical for the simultaneous analysis of rhodium and iridium because of the variation of molar absorptivity with concentration.

The stannous halide reactions were expected to form two homologous series with rhodium and iridium of increasing stability and sensitivity. Maximum absorbancy peaks also were expected to shift toward longer wave lengths in going from chloride to iodide complexes. The reaction with rhodium showed the expected increase in sensitivity but the absorbancy peaks occurred at 475 mμ, 429 mμ, and 460 mμ in going from chloride to iodide reagent. All three solutions were stable over long periods of time if oxidation by light was avoided. With iridium, the sensitivities are of the order: Br$^-$ > Cl$^-$ > I$^-$; the stabilities are of the order: I$^-$ > Br$^-$ > Cl$^-$, again if oxidation by light is avoided. Absorbancy peaks are at 360 mμ for Cl$^-$, 402 mμ for Br$^-$,

nd 446 mμ for I$^-$. The reaction of the stannous halide reagents with platinum(II) urther indicates the failure of the stannous halides to form homologous series of omplexes with platinum group metals. The stannous chloride complex has a maximum absorbancy at 403 mμ and a molar absorptivity of $1.5 \cdot 10^4$, the stannous romide complex has a maximum absorbancy at 463 mμ and a molar absorptivity of $3 \cdot 10^3$, but no absorbancy maximum was obtainable with the stannous iodide omplex which rapidly increases in molar absorptivity as the wavelength is decreased elow 385 mμ. An explanation of the anomalies of the series must await the determination of the structure and mechanism of reaction of the complexes.

The molar absorptivity of the stannous bromide complex of iridium is about three mes greater than that for the stannous iodide complex. Working ranges are 0.5–3.0 .p.m. and 0.8–11.7 p.p.m., respectively. The two methods give similar curves that il to follow Beer's law; standard and average deviations are also similar —1.2% nd 0.9%, respectively. Some advantages of the stannous iodide method are less ensitivity to the matrix acid, the heating period for color development, and sulfuric cid. The complex with stannous bromide also showed a small increase in absorbancy uring the first two hours after development, but the major advantage of the stannous dide method is the use of potassium iodide and hydrochloric acid instead of hydrobromic acid, which requires redistillation and forms a more unstable reagent with annous chloride than does hydrochloric acid.

SUMMARY

idium ions react with tin(II) iodide reagent to form a stable complex with an absorption maximum at 446 mμ. Beer's law is not obeyed but the reaction is reproducible and the absorbancy is oportional to iridium concentration with an accuracy of $\pm0.9\%$ over the range 0.8–11.7 p.p.m. rior separation of iridium from rhodium and other transition metals is necessary. The procedure mpares favorably with the tin(II) bromide method. The tin(II) halide reactions with platinum oup metals are shown to diverge from true homologous series.

RÉSUMÉ

iridium peut réagir avec l'iodure d'étain(II) pour donner un complexe stable, avec un maximum absorption à 446 mμ. Cette réaction permet d'effectuer un dosage spectrophotométrique de cet ément. Une séparation d'avec le rhodium et d'autres métaux de transition est nécessaire.

ZUSAMMENFASSUNG

eschreibung einer Untersuchung über die spektrophotometrische Bestimmung von Iridium rch Umsetzung mit Zinn(II)-jodid. Platin-und Übergangsmetalle müssen vorher abgetrennt erden.

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SPECTROPHOTOMETRIC DETERMINATION OF COBALT WITH 1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID

E. JACOBSEN AND A. R. SELMER-OLSEN

University of Oslo, Chemical Institute A, Blindern (Norway)

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INTRODUCTION

1,2-Diaminocyclohexanetetraacetic acid (Complexone IV) forms very stable complexes with certain metals[1]. Some of the complexes are coloured and consequently complexone IV has been used as the reagent in the photometric analysis of copper[2-4], manganese[5] and iron[6-8]. MARTINEZ AND MENDOZA[9] recommend complexone IV for photometric determination of cobalt. In this method the divalent cobalt complex is oxidised to a violet chelate by hydrogen peroxide in a solution of pH 7.5–9.5. In this alkaline medium, however, several other metals form coloured complexes which will interfere. The present paper describes a similar photometric method for the determination of cobalt using complexone IV in acid solution. In this medium only large amounts of chromium cause interference. The composition and stability of the trivalent cobalt complex have also been determined.

INSTRUMENTS AND REAGENTS

Apparatus

A Zeiss spectrophotometer Model PMQ II with 1.000- and 5.000-cm glass cells was used for the determination of optical densities. The pH of all solutions was measured with a Beckman Zeromatic pH meter.

Reagents

All chemicals used were of reagent grade except for the 1,2-diaminocyclohexanetetraacetic acid which was a purum product obtained from FLUKA. Stock solutions of cobalt and copper were prepared by dissolving the appropriate amounts of $Co(NO_3)_2 \cdot 6\ H_2O$ and $CuSO_4 \cdot 5\ H_2O$ in water, and standardized by electrolysis. The cobalt and the copper solutions were found to be $1.748 \cdot 10^{-2}\ M$ and $1.76 \cdot 10^{-2}\ M$, respectively. The complexone IV stock solutions were prepared by dissolving 17.336 g of 1,2-diaminocyclohexanetetraacetic acid and 4 g of sodium hydroxide in water and diluting to 500 ml. The molarity was checked by titration of a standard zinc solution using Eriochrome Black T as indicator and found to be 0.09592 M. Less concentrated standard solutions of the reagent were prepared by appropriate dilution. An acetic acid/sodium acetate buffer was prepared by dissolving 54.4 g of $CH_3COONa \cdot 3\ H_2O$ and 23 ml of acetic acid ($d = 1.05$) in distilled water and diluting to 1 l. The pH of this buffer was 4.65.

EXPERIMENTAL

.bsorption curves

MARTINEZ AND MENDOZA[9] prepared the cobalt complex by addition of hydrogen
eroxide to solutions of pH 7.5–9.5 containing cobalt ions and excess reagent, and
eating the solutions to 40°. Preliminary experiments showed that the colour dis-
ppeared slowly if the solutions were heated above this temperature. In acid solutions,
owever, the colour intensity was independent of the temperature and time of heating.
Hence, an acetate buffer seemed to be a more convenient medium for the preparation
f the cobalt complex.
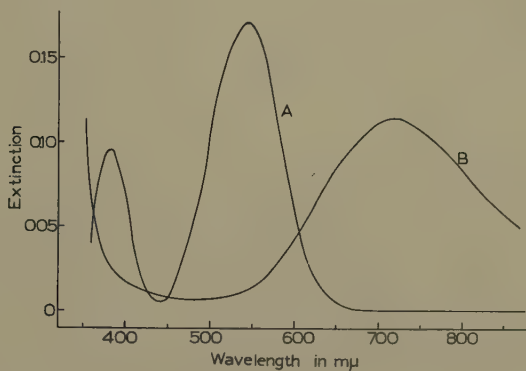
ig. 1. Absorption curves of trivalent cobalt and copper complexes with complexone IV in acetate
buffer of pH 4.65. A: $5.68 \cdot 10^{-4}$ M cobalt, B: $1.05 \cdot 10^{-3}$ M copper.
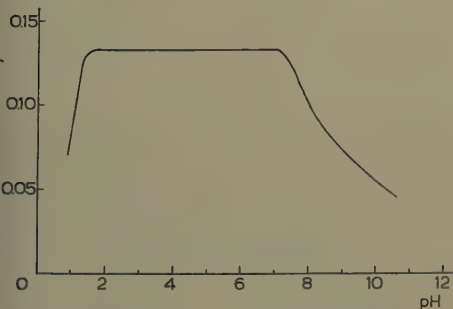
ig. 2. Effect of pH on the oxidation of the
cobalt–complexone IV complex.
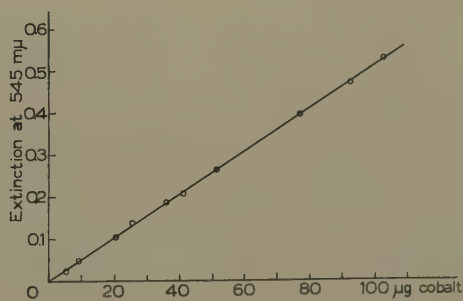
Fig. 3. Standard curve of the cobalt(III)–com-
plexone IV complex measured against distilled
water.

An absorption curve of the violet cobalt complex measured against distilled water
plotted in Fig. 1. The solution was prepared by addition of 30% hydrogen peroxide
a buffer of pH 4.65 containing cobalt and excess reagent. The violet colour was
eveloped by boiling the solution gently for 10 min. The curve exhibit maxima at
30 and 545 mμ respectively and the optical densities measured at these maxima were
und to be constant for several weeks.

Effect of pH

In order to study the effect of pH on the colour reaction, buffers of different pH were prepared. The same amounts of cobalt, excess reagent and 30% hydrogen peroxide were added to each buffer and the solution was boiled for 10 min. After dilution to constant volume the absorption curves were recorded. Absorption curves obtained from solutions of pH below 9 had distinct maxima at 380 and 545 mμ respectively. In more alkaline solution the extinction at 545 mμ decreased with increasing pH. Both maxima disappeared completely at pH 11. The extinction measured at 545 mμ are plotted against pH in Fig. 2.

The colour intensity had its maximum value in the pH region 1.5 to 7. In this pH range the optical densities were constant, and independent of pH and the time elapsed from mixing the solution. The decrease in the extinctions in alkaline solutions is probably due to decomposition of the reagent during the oxidation with hydrogen peroxide.

Beer's law

For the verification of Beer's law the optical densities were measured for a number of cobalt solutions. The solutions were prepared by addition of 10 ml of the complexone IV stock solution, 5 ml of 30% hydrogen peroxide and different amounts of the standard cobalt solution to 10 ml of acetate buffer. The solutions were boiled gently for 10 min and then diluted to 100 ml. The optical densities at 545 mμ are plotted against the cobalt concentration in Fig. 3. The system was found to obey Beer's law in the concentration range 1 to 100 μg of cobalt per ml.

The molar extinction coefficient of the cobalt complex is 305.

Interfering ions

Provided that excess reagent is present colourless ions do not interfere in the determination of cobalt. Ferric iron and manganese which interfere seriously in the alkaline medium recommended by MARTINEZ AND MENDOZA[9], cause no interference when acetate buffer of pH 4.6 is used.

Chromium forms a light green solution with complexone IV which is quantitatively converted to a violet complex when the solution is heated or exposed to the air for some hours. Chromate is reduced to the same violet complex when a solution containing excess reagent is heated with hydrogen peroxide. This violet complex which has a maximum absorption at 540 mμ and a molar extinction coefficient of about 250 interferes seriously in the determination of cobalt. The interference from small amounts of trivalent chromium can be avoided by measuring the optical density against an aliquot containing exactly the same amount of all ions except hydrogen peroxide. The blank should be boiled gently for 10 min in order to convert the chromium completely to the violet complex.

Nickel and copper form blue coloured complexes with the reagent and they give a small contribution to the optical density at 545 mμ. The absorption curves of these two complexes do not change when the solution is heated or oxidized with hydrogen peroxide. Hence the interference from nickel and copper may be avoided by measuring the absorption against a blank as described above.

The absorption curve of the copper complex is plotted in Fig. 1. The curve has a maximum at 720 mμ at which wavelength the cobalt complex does not give any

absorbance. Measurements of the optical densities of various concentrations of the copper complex showed that Beer's law is obeyed at both 545 and 720 mμ. Thus it is possible to determine the copper concentration by measuring the extinction at 720 mμ and then calculate its contribution to the absorbance at 545 mμ.

In Table I the extinctions measured against distilled water at 720 and 545 mμ of mixtures of copper and cobalt in the presence of excess reagent are reported. The theoretical extinctions and the absorbance of copper at 545 mμ were taken from standard curves. The solutions were prepared by mixing different amounts of copper and cobalt in acetate buffer. Excess reagent and 30% hydrogen peroxide were added and the solutions boiled gently for 10 min. As seen from the Table the concentration of cobalt and copper can be determined in the same solution with an experimental error of 2%.

TABLE I

PHOTOMETRIC DETERMINATION OF COBALT IN PRESENCE OF COPPER

Molarity	E theoretical		E measured		E of Cu at 545 mμ	E of Co at 545 mμ	Error %	
	Cu 720 mμ	Co 545 mμ	720 mμ	545 mμ			Cu	Co
$3.50 \cdot 10^{-4}$ Cu $3.50 \cdot 10^{-4}$ Co	0.192	0.520	0.194	0.529	0.019	0.510	+1.0	—1.9
$5.28 \cdot 10^{-4}$ Cu $3.50 \cdot 10^{-4}$ Co	0.289	0.520	0.293	0.547	0.029	0.518	+1.4	—0.4
$7.92 \cdot 10^{-4}$ Cu $3.50 \cdot 10^{-4}$ Co	0.432	0.520	0.433	0.553	0.042	0.511	+0.2	—1.9

The composition of the cobalt complex

MARTINEZ AND MENDOZA[9] suggest that the colour reaction is due to a peroxide complex or, more probably, that cobalt is oxidized to the trivalent state by hydrogen peroxide. They do not, however, give any evidence of the composition or oxidation state of the complex.

Our experiments showed that the colour reaction is independent of the kind of oxidizing agent. The same colour and absorption curve were obtained by heating solutions of the divalent complex with hydrogen peroxide or by addition of lead dioxide or potassium permanganate to the solutions at room temperature. Exactly the same absorption curve was also obtained by anodic oxidation of the divalent complex or by addition of complexone IV to solutions of sodium cobaltinitrite. These experiments indicate that the violet complex consists of complexone IV and cobalt in its trivalent state.

For the evaluation of the composition of the complex JOB's method[10] was employed. Different ratios of cobalt and reagent in acetate buffer were oxidized with hydrogen peroxide, and the solutions containing a constant total concentration of reactants were diluted to constant volume. The optical densities at 545 mμ were measured and plotted against the ratio [Co]/[Co] + [R]. A maximum, obtained where the cobalt and the reagent were present in the ratio 1 : 1, indicated the formula Co(III)R. The

experiments were repeated using lead dioxide as oxidizing agent and the same maximum corresponding to the ratio 1 : 1 was obtained.

Similar studies using the molar ratio method[11] yielded an identical composition for the complex.

The stability of the cobalt(III) complex

It was not possible to evaluate the stability of the cobalt(III) complex by JOB's method of continuous variation. Some of the reagent was decomposed by the oxidation with hydrogen peroxide leading to low values for the optical densities of solutions containing excess cobalt. An indirect spectrophotometric method described by HUGHES AND MARTELL[12] was, however, found to be useful in the calculation of the stability constant.

The method is based upon the displacement of one ion by another, according to the equilibrium:

$$MR + M' \rightleftharpoons M'R + M$$

$$K' = \frac{K_{M'R}}{K_{MR}} = \frac{[M'R]\,[M]}{[MR]\,[M']}$$

where [] represent the molar concentrations, R the chelating agent and K' the displacement equilibrium constant. The determination of K', which is equal to the ratio of the stability constants of M'R and MR leads directly to a calculation of the stability constant of one metal chelate (MR) if that of the other (M'R) is known. If both metals form 1 : 1 complexes with the reagent as in the equation above, the exact concentration of the reagent need not be considered. Hence, the method should be applicable to 1 : 1 complexes even if some reagent is decomposed during the preparation of the solutions.

Trivalent cobalt and copper ions form 1 : 1 complexes with complexone IV and as indicated in the preceding section, the concentration of these two chelates can be determined in presence of each other. The stability constant of the copper chelate has been determined previously[1]. Consequently the displacement method can be used in the calculation of the stability of the cobalt(III) complex.

Solutions containing cobalt and a slight excess of reagent were oxidized with hydrogen peroxide following the procedure outlined above. A known amount of copper was then added and the solutions were diluted to constant volume. After two days of standing the absorption of the copper complex at 720 mμ had increased to its maximum value, indicating equilibrium in the displacement reaction, and the optical densities at 545 and 720 mμ were measured. The optical densities were corrected for the absorption of uncomplexed metals as described by HUGHES AND MARTELL[12] and the corresponding concentrations of the two metal complexes (MR and M'R in the equation above) were determined from standard curves. The molar extinction coefficients for uncomplexed metals at the two wave lengths and for the copper complex at 545 mμ were taken from absorption measurements on pure substances. The concentration of uncomplexed metals (M and M') was taken as the difference between the total concentration of the metal species and the concentration of the respective metal complex (MR and M'R)

The displacement equilibrium constant K' was then calculated and $K_{\text{Co(III)R}}$

btained from the equation $K_{Co(III)R} = K_{CuR}/K'$. The results are given in Table II. All measurements were made at 20° in solutions with ionic strength 0.08. A mean value of the stability constant $K_{Co(III)R} = 8.5 \cdot 10^{21}$ was obtained when the value of og K_{CuR} was taken equal to 21.30 as determined by SCHWARZENBACH[1].

TABLE II

DETERMINATION OF THE STABILITY CONSTANT OF COBALT(III)–COMPLEXONE IV

Total molar concentration × 10⁴		Extinction measured		Molar concentration found × 10⁴				$\log K_{Co(III)R}$
Co	Cu	720 mμ	545 mμ	CuR	Cu(II)	Co(III)R	Co(III)	
5.24	4.40	0.127	0.679	1.82	2.58	4.42	0.82	22.08
3.52	4.37	0.093	0.404	1.26	2.27	2.68	1.69	21.76
6.16	5.24	0.082	0.184	0.40	5.76	1.05	4.20	21.85

Mean 21.9 ± 0.2

SUMMARY

obalt(III) forms a water-soluble complex with complexone IV. The violet complex has an absorbance maximum at 545 mμ and obeys Beer's law from 1 to 100 μg cobalt per ml. The complex is easily prepared and a procedure for the spectrophotometric determination of cobalt in acid medium is given. In this method only large amounts of chromium cause significant interference. The complex contains the cobalt and the reagent in a ratio of 1 : 1, the molar extinction coefficient is 305 and the stability constant of the complex is $8.5 \cdot 10^{21}$.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du cobalt au moyen du complexon V (acide diamino-1,2-cyclohexanetétracétique), et addition de peroxyde d'hydrogène pour obtenir e complexe violet de cobalt(III), très stable. En milieu acide, seul le chrome en forte concentration eut gêner.

ZUSAMMENFASSUNG

eschreibung einer spektrophotometrischen Methode zur Bestimmung von Kobalt mit Komplexon V und Wasserstoffperoxyd, wobei der sehr stabile, violett gefärbte Kobalt(III) Komplex entsteht. Die Reaktion wird in saurer Lösung ausgeführt, in der nur grössere Mengen Chrom störend wirken.

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VOLTAMMETRY AT INERT ELECTRODES

II. CORRELATION OF EXPERIMENTAL RESULTS WITH THEORY FOR VOLTAGE AND CONTROLLED POTENTIAL SCANNING, CONTROLLED POTENTIAL ELECTROLYSIS, AND CHRONOPOTENTIOMETRIC TECHNIQUES. OXIDATION OF FERROCYANIDE AND o-DIANISIDINE AT BORON CARBIDE ELECTRODES

THEODORE R. MUELLER AND RALPH N. ADAMS

Department of Chemistry, University of Kansas, Lawrence, Kansas (U.S.A.)

Data were presented in previous communications[1,2] which demonstrated the analytical utility of boron carbide (B_4C, "Norbide", Norton Company, Worcester, Mass.) electrodes. The purpose of the present study is to determine the adherence of experimental data at B_4C electrodes to fundamental current–voltage relationships. Data for these studies were obtained by employing voltage (E) and controlled potential (P) scanning, constant potential electrolysis, and chronopotentiometry. The equations upon which this work is based are given in Table I. Equations in this table apply only to results obtained under conditions of semi-infinite linear diffusion to a plane electrode, where only one electrode process is possible, and where both oxidized and reduced forms of the electroactive species are soluble in the solution. Conditions under which eqns. (1) and (2) are applicable are restricted further to electrode processes whose rate is mass transport controlled. Constant potential electrolysis, for purposes

TABLE I

EQUATIONS FORMING THE BASIS OF THIS INVESTIGATION

Experimental conditions	*Pertinent equation*	
Electrode potential varies linearly with time	$i_p = kn^{3/2}v^{1/2}D^{1/2}C^b A$	(1)
Correction of i_p (approx.) for IR drop when *applied voltage* varies linearly with time	$i_{p(\text{true})} = i_{p(\text{exper})}\,(1 + Ri_p/\Delta E)^{1/2}$	(2)
Constant potential electrolysis	$i_t\, t^{1/2} = \dfrac{nFAC^b\, D^{1/2}}{\pi^{1/2}}$	(3)
Constant current electrolysis (chronopotentiometry)	$iT^{1/2} = \dfrac{nFAC^b\, D^{1/2}\, \pi^{1/2}}{2}$	(4)

Note: The derivation of these equations and references to the original literature may be found in ref.[12].

f this study, is always carried out at potentials which insure mass transport control.
n chronopotentiometry, the process is likewise mass transport controlled at the
ransition time.

The validity of eqns. (3) and (4) is seemingly well established at conventional
lectrodes. A number of investigators have verified the dependence of the peak current
n some or all of the parameters in eqn. (1) at rapid scan rates, but stringent tests of
ₚ dependence on all of these parameters have not been reported, to the best of our
nowledge, at a given solid electrode for polarization rates below 1 V/min. Since the
rimary purpose of this study is to demonstrate the behaviour of B_4C electrodes,
ttempts were made to eliminate uncertainties, experimental or theoretical, which
vould detract from this goal. A method, which does not depend upon a knowledge
f the electrode area, diffusion coefficient, or concentration of electroactive species,
s described for the experimental verification of the constant, k, in the RANDLES-
EVCIK[3,4] equation for the peak current (eqn. 1). Since eqns. (1), (3), and (4) are
ased on the same fundamental postulates, it is possible to correlate results obtained
y the different techniques and thus arrive at an evaluation of the electrode apart
rom errors or uncertainties in the postulates or in the absolute values of C^b, D, or A.
ince the linear diffusion equations offer the simplest mathematical formulations, this
node of mass transport was chosen for purposes of this investigation.

Demonstration of the internal consistency of the various linear diffusion equations
hould make it possible to assess the validity of eqn. (1) at slow polarization rates.
n this work, the diffusion coefficients given by VON STACKELBERG et al.[5] were used.
These D-values were calculated from eqn. (1). RULFS[6] and MACERO[7] have determined
) for Cd^{+2} in 0.1 M KCl by non-electrochemical means. REILLEY et al.[8], using
hronopotentiometry, have calculated this same D. $D^{1/2}$-values for Cd^{+2} determined
y these four investigators vary by less than 1% from the mean value and show a
naximum spread of 1.9% compared to the lowest value. The value determined by
ON STACKELBERG and coworkers is only 0.7% higher than the mean. In a previous
ommunication[2], it was shown that areas of B_4C electrodes calculated on the basis
f D-values for ferrocyanide (FeoCy) given by VON STACKELBERG et al. agree with
nose calculated on the basis of their D-values for ferricyanide within less than 1%,
nd with projected geometric areas as well as these could be determined. It is assumed,
herefore, that it should be possible to determine the absolute validity of eqn. (1)
vithin about $\pm 2\%$ on the basis of present knowledge of D-values.

From the values of k, the slopes of current−voltage curves and chronopotentio-
rams, constancy of $E_{1/2}$ with current density and concentration of electroactive
pecies, and the relationship between $E_{p/2}$, $E_{1/2}$, and $E^{o'}$, certain conclusions are
eached concerning the reversibility of the oxidation of FeoCy in KCl solutions at
₄C electrodes. The oxidation of o-dianisidine in 1 M H_2SO_4 is included to show the
pplicability of the techniques employed to a reversible, 2-electron process.

The quantities i_p and $(it^{1/2})$ may be related if the potential of the electrode for
ne determination of the latter quantity is adjusted to a value more cathodic (or more
nodic in the case of oxidations) than the potential at which the peak current
measured. Thus, simultaneous solution of eqns. (1) and (3) gives

$$i_p = (it^{1/2}) \frac{(nv\pi)^{1/2}}{F} k \qquad\qquad (5)$$

If i_p is expressed in μA, $(it^{1/2})$ in $\mu A\text{-sec}^{1/2}$, and the expression rearranged, the equation becomes

$$9.45 \cdot \frac{i_p}{(it^{1/2})n^{1/2}} = k \cdot 10^{-5} \tag{6}$$

for scan rates of 200 mV/min.

If the same experimental conditions are used for the determination of $(it^{1/2})$, the corresponding $(iT^{1/2})$ from chronopotentiometric measurement should be

$$(iT^{1/2}) = (it^{1/2}) \frac{\pi}{2} \tag{7}$$

Eqns. (5), (6) and (7) are dimensionally correct.

From eqn. (5) it can be seen that the numerical value of the RANDLES–SEVCIK constant can be determined experimentally without knowledge of C^b, D, or A when n is known. The value of k at $25°$ deduced from calculations of RANDLES[3] and NICHOLSON[9] is about $2.72 \cdot 10^5$. MATSUDA AND AYABE[10] calculated 2.69. SEVCIK found 2.17. STREULI AND COOKE[11], using a shielded Hg pool electrode, report values of k in agreement with SEVCIK's value, but their k's required a knowledge of D and an extraneous factor, m, which is not defined. DELAHAY[12] has selected the value 2.72 as the more reliable. Constancy of experimental values and comparison with this k should provide a basis for the evaluation of an electrode. Under proper conditions, the oxidation of ferrocyanide on the reduction of ferricyanide in KCl solutions can be used as a reliable test system. If it can be established by independent methods that the electrochemical redox reaction conforms to the conditions for which eqns. (1), (3) and (4) are applicable, the interrelation of data obtained by a scanning technique and that by either controlled potential electrolysis or chronopotentiometry permits the determination of n.

Shape of the current–voltage curve and relationship between $E_{p/2}$ and $E_{1/2}$

The shape of the c–V curve (P-scan) is determined from the reciprocal slope of a plot of $\log [(i_p-i)/i]$ vs. E. Such a plot is comparable to that of $\log [(i_d-i)/i]$ vs. E in conventional polarography. The potential at which the log term becomes zero coincides with the potential $E_{p/2}$, and the reciprocal slope for a mass transport controlled process is $0.056/n$V. To date, no such evaluation of the slope is known to exist in the literature, although these conclusions are readily deduced from the work of RANDLES[3]. Since a number of rather vague statements appear in the literature concerning the relationship of $E_{p/2}$ to $E_{1/2}$ (or $E_{1/4}$ in chronopotentiometry) and E_p and concerning the slope of peak-type current–voltage curves a derivation of the slope is given in the Appendix. Reference to the excellent paper of MATSUDA AND AYABE[10] should clarify the potential relationships.

<div align="center">EXPERIMENTAL</div>

The B_4C electrodes and shields of masking tape for linear diffusion studies were described elsewhere[2]. The same three electrodes were used although the shields were changed as required. Mass transport by semi-infinite linear diffusion was approximated with the shields and checked by performing controlled potential electrolyses on a solution of potassium ferrocyanide in potassium chloride supporting electrolyte. The current–time curves were analyzed for constancy of the product $(it^{1/2})$. If this

roduct was not constant, the electrode was repositioned and another current–time
urve recorded. The procedure was repeated until $(it^{1/2})$ was constant for a minimum
f 90 sec, a time sufficient to record the c–V curve at 200 mV/min.

Current–voltage curves at stationary electrodes in unstirred solution were recorded
sing either the Leeds and Northrup Model E Electrochemograph (ECG) or a con-
olled potential scanning instrument. The controlled potential scanner was based on
circuit published by BOOMAN[13]. The description of a more refined instrument by
ELLEY, JONES AND FISHER[14] and a description of the controlled potential technique
s applied to dropping mercury polarography has already appeared. The design and
perational features of the instrument used in the present work is described else-
here[15]. This instrument was used also for the controlled potential electrolyses and
s a constant current source for chronopotentiometry. The potential–time curves
ere recorded on a Speedomax G recorder with a chart speed of 8 in./min and a full-
cale balance time of 1 sec. An L and N Model 7664 pH Meter was used as a high im-
edance buffer amplifier in the measurement of electrode potentials. Its output was
alibrated against an L and N K-3 potentiometer.

Apparatus for chronopotentiometric studies was conventional. The constant current
as known to within 0.1%. Transition times and $E_{T/4}$ values were evaluated by
raphic means. To keep the chart reading error less than 1%, transition times were
rranged to be at least 6 sec.

Background currents for E and P scanning were determined by recording the c–V
rves on solutions of the background electrolyte. The residual current contributions
the peak current ranged from 0.07 to 0.6 μA on the polished electrode to 0.1 to 0.9
A on the rough specimens, the magnitude being dependent upon the supporting
ectrolyte used. Excellent constancy of the residual current was obtained during the
urse of a run. The magnitude of the residual current is nearly identical for station-
ry, shielded electrodes and for unshielded, rotated ($>$0 to 30 r.p.s.) disc electrodes[16].

All data are reported at 25 $\pm$ 0.1°. All potentials are referred to the saturated
alomel electrode (S.C.E.) at 25°. Cell resistances were measured with an AC(1000
p.s.) conductivity bridge. Cell design, electrode mountings, and additional descrip-
on of experimental technique may be found in a previous publication[2].

hemicals and reagents

$K_4Fe(CN)_6 \cdot 3\ H_2O$ and all other inorganic chemicals were Analytical Reagent Grade
nd used without further purification. The o-dianisidine was obtained from E. I. du-
ont de Nemours and Co. through the courtesy of Mr. JOHN TINKER. Polarographic
lutions were prepared from aliquots of stock solutions of known concentration or
om weighed quantities of the solids dissolved in N_2-deaerated, distilled water.

RESULTS AND DISCUSSION

order to evaluate the B_4C electrode it was necessary to select a test system whose
ectrochemical behaviour at solid electrodes was well established. Examination of
e literature revealed that the systems most extensively studied were ferrocyanide
eoCy) and ferricyanide (FeiCy) in KCl. The oxidation of FeoCy or the reduction of
eiCy can involve only one electron, polarographic diffusion coefficients are known[5],
th oxidized and reduced forms are soluble, and the electrode reactions take place
potentials where a solid electrode should find its optimum utility. Although less

than ideal, the oxydation of FeoCy in KCl solutions was chosen as the basis for the present study.

Voltage and controlled potential scanning

The majority of the data on the FeoCy system was obtained by conventional scanning techniques using the Electro-Chemograph. It was deemed advisable, therefore, to ascertain whether or not this data, corrected by means of eqn. (2), was consistent with that obtained by the controlled potential technique. A solution of FeoCy in $1.5\ M$ KCl was prepared by dissolving a few crystals of solid potassium ferrocyanide in the KCl. A single chronopotentiogram was recorded. From the product $iT^{1/2}$, the current range for recording the c–V curve was determined. A polarogram was recorded using conventional (E) scanning. The cell circuit resistance was 330 ohm. The polarogram gave an i_p of 128 μA and an $E_{p/2}$ of $+0.252$ V. Corrected by means of

TABLE II

COMPARISON OF PEAK CURRENTS OBTAINED BY E- AND P-SCAN

Oxidation of $K_4Fe(CN)_6$ in $1.5\ M$ KCl

1 $K_4Fe(CN)_6$ conc. $\cdot 10^4$	2^a $i_p(\mu A)$ $E_{200}{}^b$	3 $i_p(\mu A)$ $P_{200}{}^c$	4 $i_p(\mu A)$ Calc.
2.04	6.20 6.24	5.85 5.75 6.00 5.98 6.00 6.01	
	Mean 6.22	5.93	6.34
4.07	13.13 13.20	11.79 12.87 12.89	
	Mean 13.16	12.52	12.65
6.11	20.80 20.55	20.25 20.28	
	Mean 20.68	20.26	18.99
10.18	32.92 32.95	32.55 32.55	
	Mean 32.93₅	32.55	31.64
20.37	64.6 64.5	64.05 65.05 64.95	
	Mean 64.65	64.68	63.31
46^d	(145.8)	(146)	143.00

a Data in Column 2 corrected for IR drop
b Conventional (E) scanning on ECG at 200 mV/min
c Controlled potential (P) scanning at 200 mV/min
d See text

qn. (2), the values were 144 μA and +0.239 V. A controlled potential scan gave $i_p =$
44 μA and an $E_{p/2} = +0.239$ V. The following day the area of the electrode was
etermined (constant potential electrolysis of 0.2 mM FeoCy in 1.5 M KCl) to be
.789 cm². From eqn. (4) and $iT^{1/2}$, the concentration of FeoCy in the former solution
was found to be 4.6 mM. These values of C^b and A, and $k = 2.72$, $D^{1/2} = 2.51 \cdot 10^{-3}$,
$T^{1/2} = 5.77 \cdot 10^{-2}$ were then substituted in eqn. (1). The calculated peak current was
43 μA. Table II shows results obtained at the same electrode two weeks earlier on
olutions of known concentration. The starred entry was calculated on the basis of
he entry immediately preceding it in the Table. Values of i_p at E_{200} have been
orrected according to eqn. (2). These results indicate that, for concentrations of
FeoCy $\geqslant$ 1.0 mM, the agreement between the two methods and with theory is within
cceptable limits.

An interesting feature of a comparison of the two scanning techniques is that, for
lectrode reactions which are not mass transport controlled, much larger discrepancies
between the two methods will become evident. The slope of the rising portion of the
polarogram will reflect not only the cell resistance but kinetic parameters as well.
This information can be used to augment other observations concerning the "polaro-
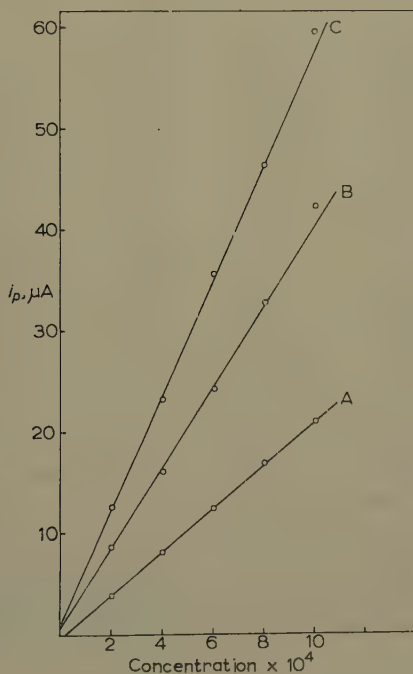
Fig. 1. Variation of i_p with ferrocyanide concentration at three scan rates. Scan rates: (A), 200;
(B), 710; (C), 1410 mV/min.

raphic reversibility" of an electrode reaction. Since there are very few reactions
which can be studied under conditions such that eqn. (1) applies, considerable care
must be exercised when interpreting data obtained by the use of conventional
polarographic instrumentation at stationary electrodes in quiet solution.

Dependence of i_p on the square root of the polarization rate was verified for scan rates of 200, 700, and 1410 mV/min for the oxidation of 5 concentrations of FeoCy in 0.5 M KCl. Peak currents were corrected according to eqn. (2). Fig. 1 is a plot of i_p vs. C^b at the three scan rates. The implications of Fig. 1 for practical analysis are clear.

Electrolysis at constant potential

For reasons which will become obvious from later discussion, it is not possible to demonstrate the dependence of i_p on $D^{1/2}$ for the FeoCy–KCl system. The dependence of $it^{1/2}$ on $D^{1/2}$ can be illustrated by data at four KCl concentrations given in Table III. The diffusion coefficients of VON STACKELBERG *et al.* were used to calculate the data in Column 4. The values of $it^{1/2}$ in 0.1 M KCl were selected arbitrarily as the basis for the calculations. The largest deviations between observed and calculated values lie within expected limits for this type of comparison[2]. Repetitive determinations of $it^{1/2}$ on the same solution, or on solutions of the same composition at the same electrode, show variations of about 0.5%.

Determination of the product ($it^{1/2}$) at *controlled potential* has shown also that values

TABLE III

DEPENDENCE OF ($it^{1/2}$) ON $D^{1/2}$

1 KCl conc. moles/l	*2* $K_4Fe(CN)_6$ conc.·10^4	*3* $it^{1/2}$ Observed	*4* $it^{1/2}$ Calculated
0.1	1.0	10.10	—
	10.0	105.2	—
0.5	1.0	10.43	10.02
	10.0	103.8	104.4
1.0	1.0	10.00	9.96
	10.0	106.8	103.7
3.0	1.0	9.96	9.86
	10.0	101.5	102.7

of this product obtained at constant *applied voltage* reported earlier[1,2] are valid. The peak in the c–V curve for the oxidation of FeoCy occurs well before the onset of the background process. It was therefore possible to use applied voltages of several hundred millivolts more anodic than the peak potential, when necessary, to compensate for IR drop when recording the i–t curve. For processes which occur close to a second process, the advantages of using controlled potential are readily appreciated.

Chronopotentiometry

Two series of runs were made on the FeoCy–KCl system. In the first series the concentration of KCl was held constant and the FeoCy concentration varied from 0.2 to 4.0 mM. Quadruplicate runs (four solutions) were made on the 0.2 and 0.4 mM, duplicate runs on the 0.6 and 1.0 mM, and single runs on the 2.0, 3.0 and 4.0 mM solutions at each current density. In the second series, the concentration of FeoCy was held constant and the KCl concentration varied from 0.05 to 4.0 M. In this case

o mM FeoCy was used in the 1.0 M KCl solution. Results of these runs are given in bles IV and V.

TABLE IV

$i_0 T^{1/2}/C$ vs. C at constant KCl concentration

$[K_4Fe(CN)_6]$ $\times 10^4$	i_0	T sec	$i_0 T^{1/2}/C$	$i_0 T^{1/2}/C$ Corrected	$i_0 T^{1/2}/C$ Mean
1	2	3	4	5	6
2.00	14.35	11.24	240.5	211.7	
	17.39	8.33	251.0	217.6	
	20.29	6.08	250.2	210.8	
	12.18	15.85	242.5	218.3	
	8.72	27.34	227.9	209.5	
	6.10	51.48	219.0	205.6	212.3
4.00	30.41	12.55	240.9	213.7	
	20.29	21.46	235.0	214.2	
	17.39	28.66	232.7	214.7	
	14.35	40.94	229.5	214.4	
	12.17	55.51	226.7	213.7	214.1
6.00	40.54	12.27	236.6	213.1	
	30.40	21.30	233.9	216.1	
	20.28	45.57	227.8	215.6	
	17.39	59.71	224.0	213.4	
	14.35	85.73	221.3	212.4	
	14.29	89.00	224.7	216.0	
	12.14	119.44	221.1	213.6	214.3
10.0	60.64	14.07	227.4	214.8	
	40.43	30.68	223.9	214.9	
	30.33	53.07	220.9	214.4	
	20.21	120.46	221.7	217.4	215.4
20.0	173.2	6.53	221.3	213.2	
	151.5	8.78	224.5	217.5	
	134.7	11.03	223.6	217.3	
	121.2	12.91	217.8	212.0	
	80.82	29.71	220.3	216.5	
	40.40	113.3	215.1	213.2	
	30.30	198.4	213.3	211.8	
	71.32	37.51	218.4	215.0	214.6
30.0	202.0	10.81	221.4	215.5	
	173.1	14.63	220.7	215.5	
	151.5	18.38	216.5	212.1	
	134.7	23.63	218.2	214.2	
	121.2	28.81	216.9	213.3	
	80.79	63.68	214.9	212.5	
	71.28	83.63	217.3	215.2	214.1
40.0	303.0	8.26	217.7		
	202.0	18.01	214.3		
	151.5	31.73	213.3		
	134.7	40.81	215.1		
	121.2	48.68	211.4		
	80.79	113.56	215.3		
	71.28	145.17	214.7		214.5

runs 1.5 M KCl, $A = 0.825$ cm^2, $E_T = +0.44$ V vs. S.C.E. Rough electrode. Mean and its ndard deviation at 95% conf. level = 214.1 ± 0.33%.

TABLE V

$i_0T^{1/2}/C$ vs. KCl CONCENTRATION AT CONSTANT FeoCy CONCENTRATION

$K_4Fe(CN)_6$ conc.·10^3	[KCl] moles/l	i_0 $\mu A/cm^2$	T, sec	$i_0T^{1/2}/C$	$i_0T^{1/2}/C$ corrected	$i_0T^{1/2}/C$ theoretical
I_i	2	3	4	5	6	7
1.00	0.05	77.52	8.47	225.6	220.8	
		55.43	16.08	222.3	218.8	
		38.76	28.05	205.3	202.7	219.7
1.00	0.10	96.90	6.14	240.3	220.2	
		77.52	9.63	240.3	224.3	
		64.53	13.67	238.1	224.7	
		55.43	18.26	236.7	225.1	
		38.76	36.10	232.9	224.6	
					Mean 223.8	218.0
1.00	0.20	96.90	6.14	240.3	216.5	
		77.52	9.63	240.3	221.3	
		64.53	13.67	238.1	215.9	
		55.43	18.18	236.7	222.9	
		38.76	35.51	231.0	221.1	
					Mean 220.8	217.6
1.00	0.30	96.90	6.3	245.2	212.4	
		77.52	9.79	242.6	216.2	
		64.53	13.67	238.1	215.9	
		55.43	17.87	234.5	215.0	
		38.76	35.12	229.8	215.9	
					Mean 215.1	216.7
1.00	1.5	96.90	6.52	247.1	213.5	
		77.52	10.10	246.5	219.5	
		64.53	14.14	242.6	219.8	
		55.43	18.64	238.9	219.0	
		38.76	36.28	233.3	219.1	
					Mean 218.2	214.4
4.00	1.0	392	4.88	216.6		
		245	12.12	213.2		
		196	19.11	214.2	0.397	
		98.00	74.4	211.3		
					Mean 213.8	214.9

$A = 0.516$ cm²; polished electrode

In all solutions except those 4.0 mM in FeoCy an increase in $i_0T^{1/2}/C^b$ was observed when the contribution of the background was not taken into account. The observed transition time reflects not only the current consumed by the faradaic process but that used for charging the double layer and, where possible, oxidizing the electrode.

ARD[17] has recently pointed out the necessity of considering an equation of the follow-
g form

$$\frac{i_0 T^{1/2}}{C^b} = \frac{nFD^{1/2}\pi^{1/2}}{2} + \frac{(C_{dl})_{avg}.\Delta E}{C^b T^{1/2}} + \frac{Q_{ox}}{C^b T^{1/2}} \tag{8}$$

the background process consists in double layer charging only, a plot of $i_0 T^{1/2}/C^b$
. $1/T^{1/2}$ will have a slope of (C_{dl})avg $\Delta E/C^b$ with an intercept of $nFD^{1/2}\pi^{1/2}/2$. This
ot was made and the corrected values of $i_0 T^{1/2}/C^b$ are given in Column 5 in Table IV
d Column 6 in Table V. The mean value is 214.1 (Table IV), in good agreement with
[4.4 calculated from eqn. (4), and with 214.5, the mean of the data 4.0 mM in FeoCy.
he improved constancy of $i_0 T^{1/2}/C^b$ with increasing concentration of electroactive
becies is not peculiar to B_4C electrodes. LINGANE[18] mentions that best results are
otained in 10 mM solutions. BARD used 5 mM solutions at platinum electrodes.
LVING AND SMITH[19], using impregnated graphite rod electrodes, also found greatest
eproducibility of $iT^{1/2}/C$ for both FeoCy and FeiCy when the concentration of these
becies was around 1.0 mM. Actually, the optimum ratio of concentration to current
ensity will depend mainly upon the roughness of the electrode. For high current
ensities and low concentrations of electroactive species, the diffusion layer at the
ansition time will be relatively thin. Since the double layer undoubtedly conforms
ery closely to the "hills and valleys" on the electrode surface, the capacity of this layer
1 a rough electrode will be large in comparison to a "smooth" electrode of the same
rojected area. As the diffusion layer thickness at the transition time increases, the
me necessary to charge the double layer is a smaller fraction of the total T. Since even
ectropolished platinum and gold electrodes are not smooth[15], it seems that the estab-
shment of optimum operating conditions must remain somewhat empirical, and
e adjusted to the particular solid electrode used.

erification of Randles' constant

The values of k in eqn. (1), obtained by applying eqn. (5) to data obtained from
ontrolled potential electrolysis at constant potential and by E and P scanning, are
sted in Table VI. From this Table it is apparent that agreement between experi-
ental results and eqn. (1) was not achieved for concentrations of KCl < 0.5 M, but
r concentrations $\geq$ 0.5 the agreement is excellent. The value of 2.72 obtained in

TABLE VI

VARIATION OF THE RANDLES–SEVCIK CONSTANT WITH KCl CONCENTRATION

$K_4Fe(CN)_6$ conc. 2 to $40 \cdot 10^{-4}$ M

KCl moles/l	$k \cdot 10^{-3}$		
	E scan	either	P scan
0.05	·1.98	—	2.15
0.10	2.06	—	2.34
0.20	2.57	—	2.52
0.30	—	—	2.62
0.50	2.72 ± 0.02[a]	—	
>0.50		2.72 ± 0.05[b]	

[a] Standard deviation of mean, 95% confidence level, 225 determinations of i_p
[b] Standard deviation of mean, 95% confidence level, 170 determinations of i_p

the 0.5 M KCl is the mean of 225 determinations at concentrations of FeoCy ranging from 0.2 to 4.0 mM, at three scan rates, using three electrodes, at temperatures ranging from 22.7° to 32.2° (corrected to 25°)[2], with all E-scan data corrected according to eqn. (2).

Clearly, the decrease in k with decreasing KCl concentration below 0.5 M cannot be the result of changing diffusion coefficients or activity of FeoCy. The ratio D_{FeiCy}/D_{FeoCy} increases slightly between 0.05 and 1.0 M KCl, but decreases again beyond 1.0 M. The change in the ratio never exceeds 2%. The decrease in k from 2.72 to 2.15 amounts to 21%. Changes in activity should be reflected equally in i_p and $(it^{1/2})$. A decrease in i_p with decreasing KCl concentration was noted also by MORRIS AND SCHEMPF[20], but these authors do not discuss its cause.

A slow step in the oxidation of FeoCy at other electrodes has been suggested by several investigators[9,21,22]. Examination of wave shapes, constancy of $E_{1/2}$ with i_0 and FeoCy concentration, and of values of k obtained by correcting E-scans with those calculated from P-scans, should give an indication of the correctness of this assumption.

The inability of eqn. (2) to give values of k which agree with those determined by P-scan (Table VI) indicates that the cell resistance is not the only factor contributing to the slope of the rising portion of the c–V curve. Since larger ΔE's cause the correction to be too small, lower values of k are predicted by eqn. (2). The values of k in 0.2 M KCl differ by less than 2% and may merely reflect experimental error. In 0.05 M KCl, however, an 8% discrepancy exists which cannot be attributed to this cause.

TABLE VII

VARIATION OF SLOPE OF POLAROGRAM WITH KCl CONCENTRATION

[$K_4Fe(CN)_6$] constant at 10^{-3} M

[KCl]	−1/slope ± 2 mv
0.05	0.066
0.10	0.065
0.20	0.058
0.30	0.059
0.50	0.056
1.00	0.055
1.5	0.057
2.0	0.056
3.0	0.057
4.0	0.054

Polished electrode, P-scan

Table VII lists data showing the dependence of the reciprocal slope of a plot of $\log[(i_p-i)/i]$ vs. E on KCl concentration at constant FeoCy concentration. Table VIII shows results of the same plot at constant KCl concentration with varying FeoCy concentration. From Table VII it may be concluded that the reaction did not become mass transport controlled until the KCl concentration reached 0.5 M. The data of Table VIII indicates that the slope of the wave is independent of FeoCy concentration at a given KCl concentration. There is no apparent difference between

e electrochemical behaviour at a polished or rough electrode. The precision of a
ngle determination at the 95% confidence level was ± 1.5% for the polished elec-
ode and ± 2.4% for the rough electrode for all determinations of i_p.

Variation of $E_{p/2}$ with KCl concentration is illustrated in Fig. 2. Values taken from
e literature are included in the plot for comparison purposes. Since the equilibrium
otential is a function of ionic strength[23], a shift in $E_{p/2}$ + 0.028 with KCl concentra-
on is expected. It will be noted, however, that, at low concentrations of KCl the
$p/2$ + 0.028 values are removed further from the equilibrium values than are the

TABLE VIII

CONSTANCY OF SLOPE OF POLAROGRAMS AT FIXED KCl CONCENTRATION

$[K_4Fe(CN)_6] \cdot 10^4$	$-1/slope$	$[K_4Fe(CN)_6]$	$-1/slope$
$[KCl]$ constant 1.5 M		$[KCl]$ constant 0.1 M	
2.0	0.053	2.0	0.066
6.0	0.056	4.0	0.066
10.0	0.056	6.0	0.066
20.0	0.056	10.0	0.067

Rough electrode, P-scan

Fig. 2. Variation of $E_{p/2}$ 0.028 V with KCl con-
centration. (●) Experimental points, mean
values; (o) Potentiometric data, Pt elec-
trode[23]; (O-) Potentiometric measurement,
graphite electrode[20]; (Q) Formal potential, Pt
electrode[21]; (Ó) Potentiometric data, Pt elec-
trode[24].
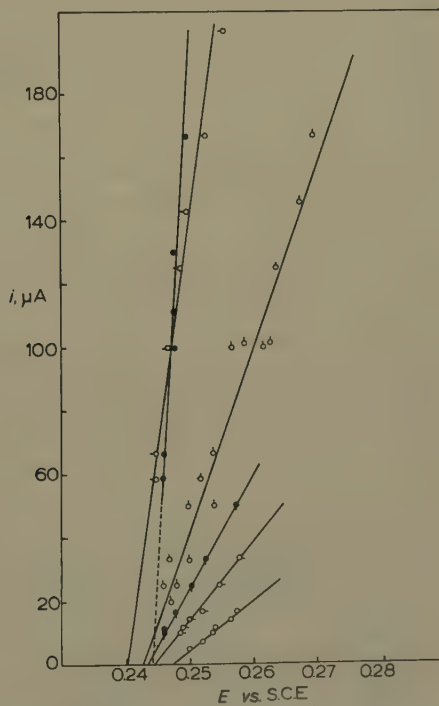
Fig. 3. Variation of $E_{1/2}$ with i_0 and ferro-
cyanide concentration. KCl concentration
constant at 1.5 M. Ferrocyanide concentra-
tion 2 (O), 4 (O-), 6 (●), 10 (Ó), 30 (-O-), and
40 (●) $\cdot 10^{-4}$ M.

corresponding potentials at higher concentrations. This shift away from equilibrium is characteristic of charge transfer controlled reactions. In addition, $E_{p/2}$ and E_p were always separated by more than 0.056 V for KCl concentrations $<0.5\ M$.

A marked shift in $E_{1/2}$ with i_0 and FeoCy concentration (Figs. 3 and 4) is evident
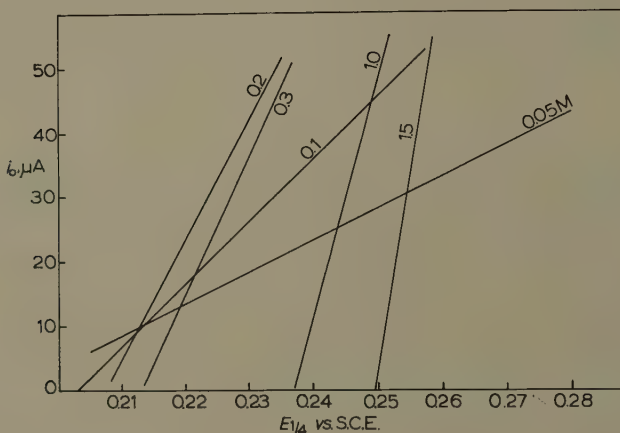
Fig. 4. Variation of $E_{1/2}$ with i_0 and KCl concentration. Numbers on lines refer to molar concentrations of KCl. Ferrocyanide concentration $10^{-3}\ M$.

also. For a "reversible" process, no shifts are predicted. For a "totally irreversible" process the following equation applies[25]:

$$E = \frac{RT}{\alpha_{na}F} \ln \frac{nFC^b k^\circ_{f,h}}{i_0} - \frac{RT}{\alpha_{na}F} \ln \left[1 - \left(\frac{t}{T} \right)^{1/2} \right] \qquad (9)$$

from which it can be seen that E shifts with both i_0 and C^b. For processes which proceed at rates such that neither classification is applicable, REINMUTH[26] has shown that a shift of E with these parameters may be expected. Data of Fig. 3 extrapolated

TABLE IX

VARIATION OF SLOPES OF CHRONOPOTENTIOGRAMS WITH i_0 AND KCl CONCENTRATION

$K_4Fe(CN)_6$ conc. $= 1 \cdot 10^{-3}\ M$. Polished electrode, $A = 0.516\ cm^2$

[KCl] moles/l	−1/slope					
	50 μA	40 μA	33.3 μA	28.6 μA	20 μA	12 μA
0.05	—	0.080	—	0.074	0.062	—
0.1	0.081	0.080	0.063	0.070	0.062	—
0.2	0.070	0.072	0.070	0.067	0.066	—
0.3	0.079	0.076	0.071	0.068	0.068	—
1.0[a]	0.064₅	—	0.059	—	0.061	0.059
1.5	0.074	0.070	0.075	0.069	0.067	—

[a] $K_4Fe(CN)_6$ conc. $= 4 \cdot 10^{-3}\ M$ (actual i divided by 4 to fit table)

$i_0 = 0$ gives values of $E_{1/4}$ in good agreement with the value $E_{p/2} + 0.028$ V from - or P-scan curves. Attention is called to the fact that the voltage axis of Fig. 3 is vided into units of only 10 mV. Experimental points have been deleted from Fig. 4 avoid confusion.

Finally, Table IX shows the values for the reciprocal slopes of plots of $\log (T^{1/2} - t^{1/2})/t^{1/2}$ vs. E for 1.0 mM FeoCy in several concentrations of KCl. Mass transport ntrol of the reaction is indicated for high concentrations of both FeoCy and KCl low current densities only.

Consideration of the data obtained by the several techniques described indicates at the oxidation of FeoCy in KCl at B_4C electrodes involves a slow electron transfer ep. The charge transfer step is rapid enough, however, so that, at slow polarization tes or low current densities, diffusion becomes the rate-determining process in high ncentrations of KCl (E- or P-scan) and high FeoCy concentrations (chronopotenti-metry). From chemical considerations, it is difficult to see, however, why this system ould show such abrupt departure from reversible behaviour. It is possible that many the effects of varying KCl concentration could be explained on the basis of changes double layer structure. The present investigation was carried out primarily to emonstrate the acceptability of B_4C electrodes for electrochemical investigations ther than for the elucidation of any specific reaction mechanism, and further study the FeoCy oxidation is necessary to establish the validity of either explanation.

The data presented in this section represents about 900 determinations collected a period of $1\frac{1}{2}$ years. The self-consistency of the data attests to the long-range producibility of B_4C electrodes and to their applicability in electrochemical in-estigations.

Dianisidine

The oxidation of o-dianisidine in 1 M sulfuric acid was carried out at rough and olished B_4C electrodes, at a large platinum foil, and at an electropolished platinum icroelectrode[15] by the chronopotentiometric method. At the rough B_4C and platinum il electrodes, $E_{1/2}$ values were $+ 0.594$ and 0.592 ± 0.002 V, respectively. At both olished electrodes a decrease in $i_0 T^{1/2}$ with increasing i_0 was noted, but $E_{1/2}$ values the same i_0 were identical at the two electrodes. Reciprocal slopes of plots of log $T^{1/2} - t^{1/2})/t^{1/2}$ vs. E were $-0.029 \pm 0.001_5$ V at the rough B_4C and platinum foil ectrodes and -0.036 at both polished electrodes. E- and P-scans at both B_4C ectrodes gave values of the RANDLES' constant, k, between 2.69 and $2.72 \cdot 10^5$ for $= 2$. Reciprocal slopes of the plot of log $[(i_p - i)/i]$ vs. E were $-0.0275 \pm 0.001_5$ V. ne relationship, $E_{p/2} + 0.028$ V $= E_p$ held within ± 0.002 V. Values of $(it^{1/2})$ and $^{1/2}$ for values of $iT^{1/2}$ extrapolated to $i = 0$ agreed with eqn. (7) within 1.5%. The ta were taken from two series of runs performed one year apart. Mean values of $/C^b A$ were identical for the two series at B_4C electrodes. The oxidation of o-dianisi-ne in 1 M sulfuric acid appears to be mass transport controlled when studied at ationary electrodes at slow scan rates.

Further study of the electrochemical behaviour of o-dianisidine in 1 M sulfuric acid ould be of interest. The compound appears to be quite stable in storage, and preci-on obtained with this compound exceeds that realized with any other electroactive ecies studied at B_4C. Perhaps this system could be used for evaluation studies in eference to the more troublesome FeoCy–KCl or FeiCy–KCl systems.

APPENDIX

Substituting the symbols defined previously and $A - 4\pi v^{2/3}t^{2/3}$ in RANDLES' eqns. (8) and (9)[3], the following relationships for the instantaneous and peak currents are obtained:

$$i_t = \frac{FC_m A n^{3/2} v^{1/2} D^{1/2}}{(0.0118)^{1/2} \cdot 10^3} \delta C_0 \qquad \text{(A 1)}$$

and

$$i_p = \frac{0.310 FC_m A n^{3/2} v^{1/2} D^{1/2}}{(0.0118)^{1/2} \cdot 10^3} \qquad \text{(A 2)}$$

Let

$$K = \frac{FC_m A n^{3/2} v^{1/2} D^{1/2}}{(0.0118)^{1/2} \cdot 10^3}. \qquad \text{(A 3)}$$

Eqns. (A 1) and (A 2) then reduce to the form

$$i_t = K\delta C_0 \qquad \text{(A1')}$$

and

$$i_p = 0.0310 K \qquad \text{(A2')}$$

Then

$$\frac{i_p - i}{i} = \frac{0.310 K - K\delta C_0}{K\delta C_0} = \frac{0.310 - \delta C_0}{\delta C_0} \qquad \text{(A 4)}$$

When the logarithm of eqn. (A 4) becomes zero, solution of this equation for δC_0 gives, $\delta C_0 = 0.155$. The abscissa (voltage coordinate) corresponding to this value of δC_0 is determined from Fig. 3 (RANDLES). It is noted that the value of the abscissa so located and the value of the abscissa corresponding to E_p ($\delta C_0 = 0.310$) are symmetric about the origin, $E_{1/2}$. The dimensionless abscissa of RANDLES converted to V gives, for E_p and $E_{p/2}$, the value $0.028\,n \pm E_{1/2}$ V. The plus sign indicates an oxidation and the minus sign a reduction. The observation concerning the peak potential has already been made by DELAHAY[12]. Since $(i_p-i)/i$ also corresponds to $0.310/2$, the value at half peak current, $E_{p/2} \pm 0.028/n = E_{1/2}$. Thus, the potential at half peak current has thermodynamic significance and is directly related to $E_{1/2}$ in conventional polarography.

Application of eqn. (A 4) for other points along the c–V curve *in the vicinity of* $E_{p/2}$ shows that, for a change of 1 unit in the logarithmic term, the voltage increment is between 0.056 and 0.057 V for a 1-electron process. A plot of log $[(i_p-i)/i]$ *vs.* E, therefore, should yield a reciprocal slope of about $0.056/n$ V, and the potential at which the logarithmic term becomes zero should be the half-peak potential.

It is advantageous experimentally to be able to attach significance to $E_{p/2}$ in that measurement of E_p is difficult. Due to rounding of the c–V curve in the vicinity of the peak, peak potentials cannot be measured with the same accuracy or precision that is possible for $E_{p/2}$. It may also be concluded that, for a "polarographically reversible" redox reaction, $E_{p/2(\text{cathodic})}$ and $E_{p/2(\text{anodic})}$ will be separated by $0.056/n$ V.

SUMMARY

An exhaustive study of linear diffusion techniques has been carried out at B_4C electrodes. In addition to proving the utility of B_4C electrodes for both practical and theoretical investigations, some novel inter-relationships between modern electrochemical techniques have been developed, and the validity of the RANDLES–SEVCIK equation has been established for slow scan rates.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'utilisation d'électrodes inertes de carbure de bore, en voltammétrie. Ils ont examiné en particulier l'oxydation du ferrocyanure et de l'o-dianisidine.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Anwendung von B_4C Elektroden bei chronopotentiometrischen Methoden. Die Eignung dieser Elektroden für elektrochemische Untersuchungen wurde durch das Studium der Oxydation von Ferrocyanid und o-Dianisidin nachgewiesen.

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SÉPARATION PAR VOLATILISATION DES RADIOISOTOPES DE MERCURE, DE PLATINE, D'IRIDIUM, D'OSMIUM ET DE RHÉNIUM FORMÉS PAR SPALLATION DANS UNE CIBLE D'OR

JEAN MERINIS ET GEORGES BOUISSIÈRES

Institut du Radium, Laboratoire Curie, Paris et Laboratoire de Physique Nucléaire, Orsay (France)

Dans le cadre de l'étude des réactions de spallation en cours à l'Institut du Radium, nous nous sommes intéressés à la séparation des isotopes de mercure, de platine, d'iridium, d'osmium et de rhénium formés dans des cibles d'or irradiées par des protons de 150 MeV au synchrocyclotron du Laboratoire Joliot–Curie à Orsay. La séparation de ce groupe d'éléments, soit par réactions de précipitation, soit par extraction par solvants, est assez délicate et le traitement d'une cible généralement laborieux. POFFE *et al.*[1] ont séparé le mercure formé dans ces cibles par distillation sous vide. Cela nous a incités à rechercher une méthode plus générale de séparation par volatilisation permettant d'isoler également les autres radioéléments formés en mettant à profit les résultats de recherches effectuées par l'un de nous[2] sur la vaporisation des chlorures d'or.

Le procédé que nous proposons consiste en un fractionnement des éléments ou de leurs chlorures, par sublimation et condensation dans un tube le long duquel est établi un gradient de température. Des procédés analogues ont été utilisés par plusieurs auteurs[3–9] pour purifier ou séparer principalement des composés organiques, soit sous vide, soit en atmosphère contrôlée.

Les feuilles d'or irradiées sont placées au point le plus chaud d'un tube de pyrex ou de quartz. Le tube est traversé, selon le cas, par un courant d'argon, d'oxygène ou de chlore. En chauffant l'or vers 700°, dans l'argon, le mercure distille et se condense dans le tube à une distance bien déterminée. A 270°, dans un courant de chlore, l'or et aussi l'osmium et le rhénium sont transformés en chlorures volatils qui se séparent dans le tube dans l'ordre de leurs températures de condensation décroissantes. En élevant ensuite lentement la température du four on isole les chlorures d'autres éléments, notamment de platine, d'iridium et de tungstène.

TECHNIQUES EXPÉRIMENTALES

Appareillage

Un tube en cuivre de 90 cm de longueur, 15 mm de diamètre extérieur, 5 mm de diamètre intérieur, est chauffé à une des extrémités par un four électrique de 500 W, et refroidi à l'autre extrémité par un serpentin de cuivre parcouru par un courant d'eau à 10° (Fig. 1). La partie centrale est calorifugée par une couche de 5 cm d'épaisseur de terre d'infusoires. On introduit dans l'âme du tube de cuivre un tube de pyrex

u de quartz d'un mètre de longueur, de 4 mm de diamètre extérieur et de 2 mm de
iamètre intérieur dont une extrémité coudée en forme d'U plonge dans un mélange
éfrigérant glace–chlorure de sodium (—15° environ). Le tube de pyrex ou de quartz
st parcouru, du point chaud vers le point froid, par un courant d'argon, d'oxygène
u de chlore soigneusement desséché, dont le débit est de 0.2 ml/sec à la pression
tmosphérique. À la sortie de l'appareil, le gaz est envoyé successivement dans deux
acons laveurs à HCl concentré puis dans un flacon laveur à HNO_3 concentré, et
nsuite évacué à l'extérieur du laboratoire.
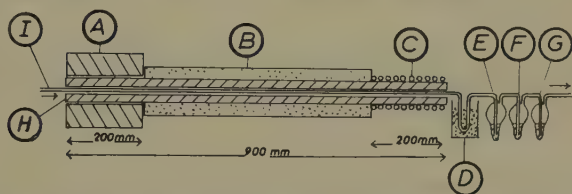
Fig. 1. A, four électrique; B, calorifuge; C, serpentin de refroidissement; D, piège à glace + NaCl;
et F, flacons laveur à HCl conc.; G, flacon laveur à HNO_3 conc; H, tube de cuivre; I, tube de
pyrex ou de quartz.
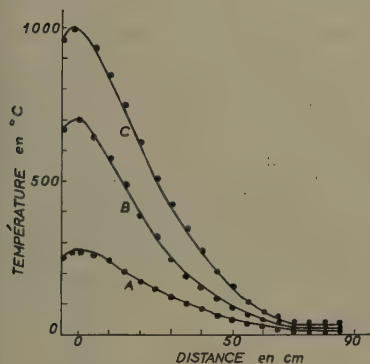
Fig. 2. Variation de la température le long du
ube. Températures du four: 270° (courbe A),
700° (courbe B), 1000° (courbe C).
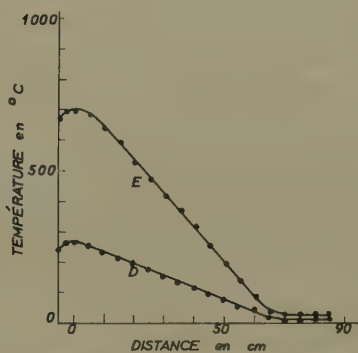
Fig. 3. Gradients de température réalisés avec
l'adjonction d'un four auxiliaire au centre du
tube.

La température à l'intérieur du tube de cuivre a été mesurée cm par cm à l'aide d'un
hermocouple. La température du four étant fixée à 270°, puis à 700° et 1000°, on
btient les trois courbes de température A, B, C (Fig. 2), le point le plus chaud du
ube étant pris comme origine des distances. On peut améliorer la linéarité des courbes
e température en chauffant légèrement le centre du tube sur 30 cm environ de lon-
ueur avec un four auxiliaire (courbes de la Fig. 3). Les températures à l'intérieur du
ube sont peu modifiées par la circulation d'un gaz à faible vitesse.

Un dispositif automatique permet de faire monter graduellement la température
u four en plusieurs heures jusqu'à une valeur limite prédéterminée.

raitement des cibles d'or irradiées

Séparation dans un courant d'argon ou d'oxygène. La feuille d'or ($15 \times 10 \times 0.01$
m) irradiée par les protons est roulée en cylindre et introduite dans le tube de pyrex
oid, à l'endroit défini par le maximum des courbes de température de la Fig. 3.

Le balayage du tube par le courant d'argon ou d'oxygène est établi, puis le four est porté à 700°. Cette température est maintenue pendant 2 à 5 h pour volatiliser le mercure.

Séparation dans un courant de chlore. Après distillation du mercure, la feuille d'or roulée est placée dans un deuxième tube de pyrex ou de quartz, et le courant de chlore établi. La température du four est fixée alors à 270°, température qui semble la plus favorable à la volatilisation de l'or à l'état de trichlorure.

La chloruration de l'or est complète après 2 à 6 h de chauffage suivant la quantité de métal présente. Les chlorures d'osmium et de rhénium sont aussi distillés dans ces conditions.

D'autres chlorures peuvent être séparés en élevant lentement la température du four jusqu'à 700° en 5 h pour les tubes de pyrex, ou jusqu'à 1000° en 8 h pour les tubes de quartz.

Localisation des produits séparés

Les tubes de verre ou de quartz sont retirés de la gaine de cuivre et découpés en fragments de 1 cm de longueur dont l'activité est mesurée avec un ensemble de comptage à scintillation muni d'un cristal à cavité, d'iodure de sodium activé au thallium de 5 cm × 5 cm. On porte sur un graphique, en fonction de la distance du point le plus chaud, l'activité de chaque portion du tube dont on peut, en se reportant à la Fig. 2, connaître approximativement la température. La courbe ainsi obtenue présente un certain nombre de pics. L'analyse à l'aide d'un compteur à scintillation associé à un sélecteur d'énergie, du rayonnement γ correspondant à chacun de ces pics, et éventuellement la mesure de la période de décroissance de l'activité, permettent de caractériser les éléments séparés. En effet parmi les nucléides formés par spallation de l'or certains, tels que ^{195}Hg, ^{195}Au, ^{196}Au, ^{188}Pt, ^{189}Ir, ^{190}Ir, ^{192}Ir, ^{185}Os et ^{183}Re sont aisément identifiables par la forme de leur spectre γ. Notons que l'or est en quantité suffisante pour être décelé visuellement.
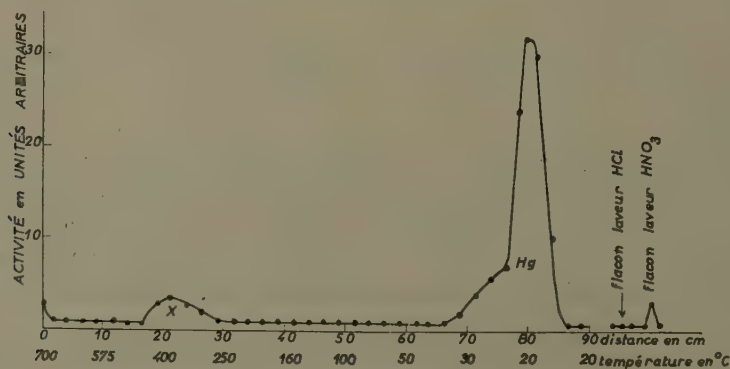
Fig. 4. Séparation de Hg (atmosphère d'argon, température du four: 700°).

RÉSULTATS EXPÉRIMENTAUX

Séparation en atmosphère d'argon ou d'oxygène

La courbe de la Fig. 4 indique la distribution de l'activité le long du tube obtenue en chauffant à 700° la cible d'or irradiée dans un courant d'argon purifié. Elle fait

pparaître un dépôt bien délimité de mercure à environ 80 cm de la feuille d'or. La
roportion de mercure extraite en deux heures est voisine de 90%; elle atteint 98%
près 5 h de chauffage. Ces rendements sont voisins de ceux obtenus par BEYDON
 al.[10] en chauffant une cible d'or à 900° sous vide.

Un radioélément en quantité trop faible pour pouvoir être identifié (période d'environ
 jours) se dépose à une vingtaine de cm du point le plus chaud; on recueille également
ne activité très faible, décroissant avec une période voisine de 200 jours, dans le flacon
veur contenant HNO_3.
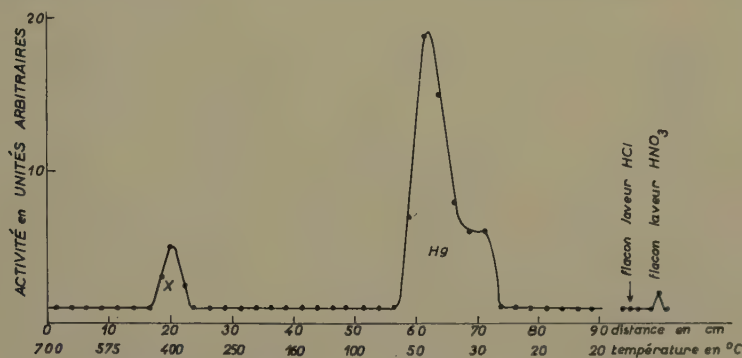
Fig. 5. Séparation de Hg (atmosphère d'oxygène, température du four: 700°).

Si l'on remplace le courant d'argon par un courant d'oxygène, le mercure est extrait
e la feuille d'or comme précédemment, mais l'activité déposée avant le mercure est
lus importante. Cela n'altère d'ailleurs pas la pureté du mercure qui est bien séparé
omme le montre la courbe de la Fig. 5.
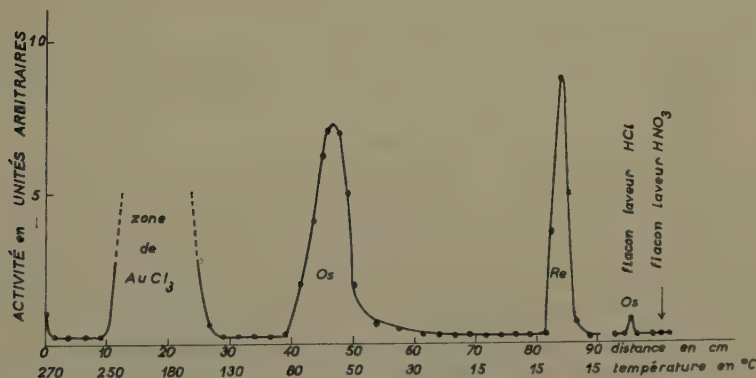
Fig. 6. Séparation de Os et Re (atmosphère de chlore, température du four: 270°).

éparation en atmosphère de chlore

Expériences à 270°. L'or, l'osmium et le rhénium donnent des chlorures qui sont
olatilisés et bien séparés (Fig. 6).

Le dépôt d'or sous forme de chlorure rouge cristallisé commence à une dizaine de cm

du point le plus chaud du tube, et s'étale sur une longueur de 15 à 20 cm. Le tétra-chlorure d'osmium, $OsCl_4$, formé se dépose à environ 50 cm. Une petite fraction d'os-mium de l'ordre de quelques pourcents est recueillie dans le flacon laveur à HCl, vraisemblablement à l'état de OsO_4. Cette fraction est plus importante si l'on n'a pas éliminé toute trace d'oxygène par un chauffage suffisant de la feuille d'or dans un courant d'argon avant d'admettre le chlore dans le tube.

Enfin, on retrouve le rhénium à 80–85 cm du point de départ, soit dans une zone où la température est d'environ 15°. Il est probablement volatilisé à l'état de $ReCl_6$ dont le point d'ébullition est inférieur à 40°.
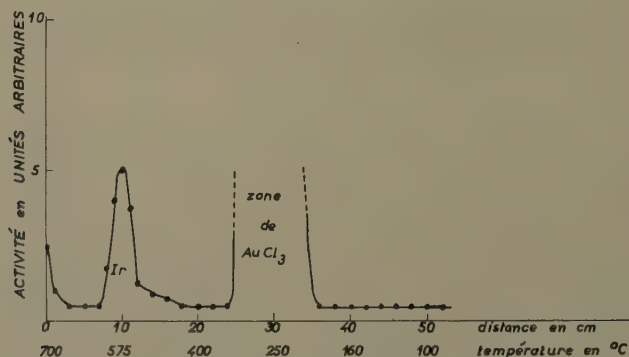
Fig. 7. Séparation de Ir (atmosphère de chlore, température du four: 700°).

Expériences à 700° et à 1000°. Après avoir effectué la chloruration de l'or à 270° comme il vient d'être indiqué ci-dessus, la température du four est portée à 700°. Dans ces conditions le chlorure d'or se déplace et se localise dans la portion du tube située à 25–35 cm environ de l'extrémité chaude du tube. L'iridium, alors volatilisé,
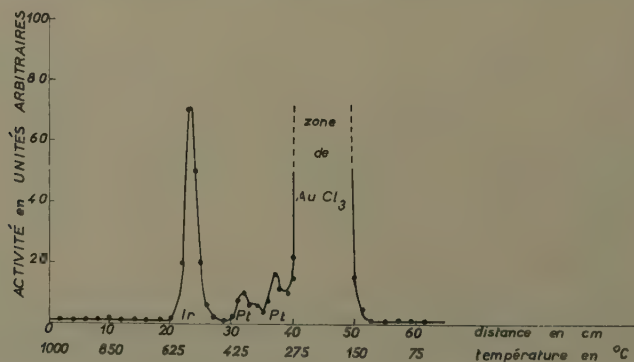
Fig. 8. Séparation de Pt et Ir (atmosphère de chlore, température du four: 1000°).

est bien isolé à une dizaine de cm de l'origine. Quant au platine, il reste au point de départ, vraisemblablement sous forme de $PtCl_2$ (Fig. 7).

Par contre, si la température du four est élevée progressivement de 270 à 1000° il se forme $PtCl_4$ qui est volatilisé et se condense à une distance d'environ 40 cm du

...oint chaud, tandis que l'iridium migre à 23–24 cm. L'or migre aussi mais cependant ...as suffisamment pour être séparé complètement du platine (Fig. 8). On pourrait ...emédier à cet inconvénient en chassant assez loin $AuCl_3$ avant de volatiliser le platine. .. suffirait pour cela de déplacer lentement dans la gaine de cuivre le tube de quartz ...ers la zone chaude, le four étant maintenu à 270°; puis, après une migration suffi-...ante de $AuCl_3$, de replacer le tube à sa position initiale avant d'élever la température ...u four de 270° à 1000°.

Il nous a paru utile de compléter ce travail par l'étude de la séparation Au, Pt, ... et W, car il serait également intéressant de rechercher les isotopes de W éventuelle-
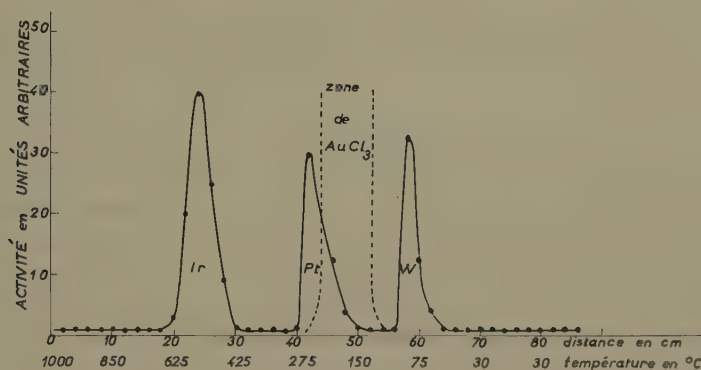
Fig. 9. Séparation de Pt, Ir et W (atmosphère de chlore, température du four: 1000°).

...ent formés par spallation de l'or. Pour faciliter la mise au point de cette séparation, ...ous avons opéré sur un mélange des métaux: or (une feuille de 15 × 10 × 0.01 mm), ...latine et tungstène (0.1 mg environ). Les échantillons de platine et de tungstène ...vaient été auparavant irradiés à la pile. Le platine était ainsi marqué par [188]Pt, et ... tungstène par [185]W. Une impureté d'iridium dans le platine a pu être décelée par ...activité de [192]Ir. La Fig. 9 montre que le tungstène est bien séparé de l'or, du platine ... de l'iridium. Il se dépose à environ 60 cm de la position initiale, sous forme de ...ristaux rouges, $WOCl_4$, formés en présence des traces d'oxygène contenues dans le ...hlore.

CONCLUSION

...a séparation des isotopes radioactifs de Hg, Pt, Ir, Os et Re formés dans une cible ...'or par spallation a été réalisée par volatilisation dans un tube le long duquel est ...abli un gradient de température. La méthode mise en oeuvre apparaît bien adaptée ... la séparation et à la purification de certains radioéléments en quantités impondé-...bles; elle ne nécessite pas l'emploi d'entraîneurs, ce qui pour certains travaux est ...ès important. Son application à divers problèmes de radiochimie est en cours.

RÉSUMÉ

Les isotopes radioactifs de mercure, platine, iridium, osmium et rhénium, produits par réactions de spallation dans l'or irradié avec des protons de 150 MeV, sont séparés sans entraîneurs par distillation dans un courant d'argon ou de chlore, et condensation dans un tube le long duquel est établi un gradient de température.

SUMMARY

The radioactive isotopes of mercury, platinum, iridium, osmium and rhenium — products of bombardment processes in gold irradiated with protons at 150 MeV — are separated cleanly by distillation in a stream of argon or chlorine and by condensation in a tube possessing a temperature gradient.

ZUSAMMENFASSUNG

Die radioaktiven Isotopen von Hg, Pt, Ir, Os und Re lassen sich durch Destillation in einem Strom von Argon oder Chlor sauber trennen, wenn die Kondensation in einer Röhre, die einen Temperaturabfall aufweist, erfolgt.

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Short Communications

Note sur la détection très sensible des gaz permanents en chromatographie gazeuse au moyen du detecteur à hélium métastable

L'idée déjà ancienne[1] du remplacement de l'argon par l'hélium pour l'analyse des gaz minéraux dont le potentiel d'ionisation est supérieur à 11.6 volts a été exploitée d'abord par BERRY[2] et tout récemment par WISEMAN[3], mais les auteurs ont toujours insisté sur la difficulté pratique d'une purification suffisante de l'hélium à moins de partir d'hélium atmosphérique très coûteux.

Nous avons obtenu récemment de très hautes sensibilités dans la détection de traces de gaz permanents au moyen d'un chromatographe Pye* standard, muni du détecteur classique de LOVELOCK[4] avec un procédé de purification extrêmement simple du gaz porteur.

Nous utilisons une colonne en verre de 1.20 m remplie de tamis moléculaires 13 A. L'hélium commercial à 99.9% traverse une colonne spirale de 8 m en acier inox de mm de diamètre intérieur remplie de tamis moléculaires 5 A et plongeant dans azote liquide (Fig. 1). Il n'y a aucun joint en matière organique en aval de la spirale.
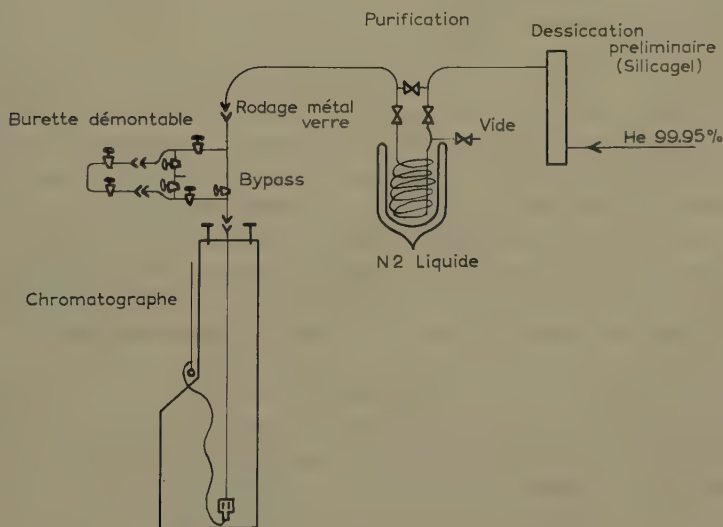
Fig. 1.

es tamis 5 A sont régénérés sur place à 300° sous vide de pompe à palettes. Le hromatographe est étuvé 24 h à 200° sous hélium pur, après régénération extérieure nergique des tamis 13 A. La sensibilité de l'appareil s'améliore pendant 2 ou 3 jours. u début nous avions déjà observé les pics négatifs et les pics en W que vient de gnaler WISEMAN.

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* Avec une tension de 1000 volts.

Il est nécessaire d'avoir au moins 9 l/h d'hélium pour éviter la diffusion des gaz atmosphériques dans le détecteur, mais un débit plus élevé est inutile.

On peut facilement déceler des teneurs de 0.1 à 1 v.p.m. avec des éprouvettes de quelques cm³. L'introduction de l'échantillon se traduit par un "à coup" positif. Fig. 2 représente un chromatogramme de traces de gaz permanents dans un composé fluoré, invisible du fait de son temps de rétention élevé.
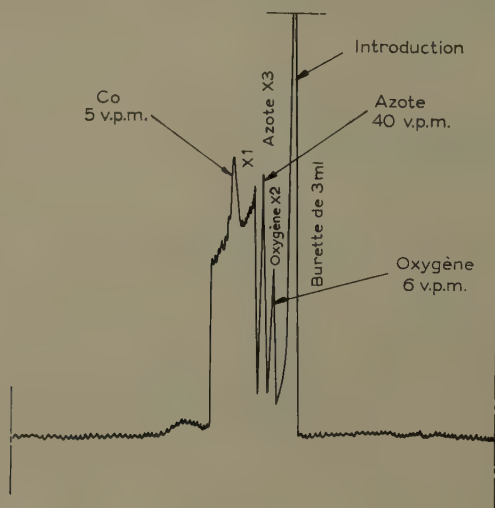
Fig. 2.

Cette méthode tire son intérêt de sa simplicité* et de son application possible à la recherche de traces d'oxyde de carbone ou d'oxygène dont l'importance industrielle est considérable. La chromatographie gazeuse fournit en particulier pour l'analyse de traces d'oxygène moléculaire une méthode de détection beaucoup plus spécifique que la plupart des méthodes actuelles faisant intervenir des réactions d'oxydation. Ce travail a été effectué dans le cadre d'un contrat avec le Commissariat Français à l'Énergie Atomique. Nous remercions sincèrement la Direction de ce Service d'avoir autorisé cette publication.

Société d'Electrochimie d'Electrometallurgie et des Acieries   JOSEPH SERPINET
Electriques d'Ugine, Centre de Recherches de Lyon,
Pierre-Benite, Rhône (France)

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* L'emploi plusieurs fois signalé du même appareil comme détecteur à mobilité d'électrons avec de l'hélium plus ou moins volontairement contaminés[5], est d'un emploi moins commode et conduit à une moindre sensibilité.

The reactions of diphenylcarbazide and diphenylcarbazone with cations

In the course of research on the stability constants of diphenylcarbazide and diphenylcarbazone complexes with B-group cations, with the object of completing the "dithizone system"[1], several interesting observations were made. These are summarized in the following paragraphs.

Reagents

Diphenylcarbazone, on titration with base, proves to be a monobasic acid; spectrophotometric determination of the partition equilibrium in the system carbon tetrachloride–water as controlled by the pH, gives for K_{diss}. the value $(2.2 \pm 0.2) \cdot 10^{-8}$, whereas diphenylcarbazide is a neutral compound. The visible spectrum of diphenylcarbazone in toluene solution shows a strong maximum at 467 mμ, and a weaker one at 565 mμ. Irradiation of the solution with UV-light makes the latter maximum increase, while the former decreases.

Complex formation

There is no agreement in the literature whether only diphenylcarbazone[2] or both the carbazide and carbazone[3,4] form metal complexes. We have shown that with some non-oxidizing cations (zinc, nickel(II), lead(II) and cadmium) colored complexes are found only with diphenylcarbazone; the carbazide does not react with them if it is freshly recrystallized from alcohol. On the other hand, oxidizing cations (mercury(I) and (II), copper(II) and iron(III)) do react with diphenylcarbazide. Subsequent acid decomposition of the extracted or precipitated compounds showed, however, that the carbazone and not the carbazide is bound. The acid solution does not react with maromic acid, which is a reagent for diphenylcarbazide[5]. Thus complex formation actually occurs with diphenylcarbazone which is first formed from the carbazide by an oxidation reaction with the cations of mercury etc. So far, we have been unable to find any diphenylcarbazide compounds alongside the carbazone complexes.

The diphenylcarbazone complexes investigated are more easily oxidized by atmospheric oxygen than is diphenylcarbazone itself.

We have established that the diphenylcarbazone complexes of mercury(I) and (II) and copper(II) are stable in the solid state; in toluene solution they decompose to form the oxidation product of diphenylcarbazone, i.e. diphenylcarbodiazone, which can be identified by means of the absorption spectrum. The other decomposition products are mercury and probably copper(I). Irradiation with UV-light accelerates such decomposition. The other investigated complexes do not show such decomposition in toluene solution.

From the Tyndall effect we concluded that diphenylcarbazone and the mercury(I) and (II) and cadmium(II) complexes are colloids in an alcohol–water solution.

Job curves and extinction measurements on solutions of the lowest metal-diphenylcarbazone complexes with varying excesses of the carbazone, prove that both

mercury(I) and (II) and nickel(II) form $1:1$ and $1:2$ compounds (M:diphenyl-carbazone), comparable to the primary and secondary dithizonates; lead(II) and zinc-(II) give only $1:2$ compounds.

The dissociation constants of the complexes, measured spectrophotometrically by using the extraction method, are several orders greater than the constants of the corresponding dithizonates. For instance:

$$\frac{(Hg^{++})_w \, (dco)^2_t}{(1:2 \text{ compl.})_t \, (H^+)^2_w} = 5.2 \cdot 10^{-6}$$

where w = water, t = toluene, and dco = diphenylcarbazone, whereas the corresponding constant for dithizone[1] in the system carbon tetrachloride–water is $1.4 \cdot 10^{-27}$.

Mercury(I) and (II) nitrate and perchlorate solutions show a strong ageing effect: the reaction of freshly prepared solutions with diphenylcarbazone decreases by 40–80% in 20 h, depending on the pH; the only possible explanation proved to be slow hydrolysis. This behaviour may be compared with that of rhodium(III) solutions[6].

For the complexes studied no linear relationship exists between K and $\lambda_{max.}$ in the visible spectrum[7].

Infrared spectra of the solid $(1:1)$ complexes of mercury(I) and (II) and cadmium-(II) (in KBr discs) do not show any absorption at $5.85\ \mu$, the wavelength of the C=O bond in diphenylcarbazone. This is an indication of M-O bonding in these complexes, with the carbazone in the enolic form.

Studies on the properties and dissociation constants of the diphenylcarbazone compounds are being continued; more detailed publication will follow in due course.

Chemical Laboratory, Free University,   E. van Dalen
Amsterdam (The Netherlands)   S. Balt

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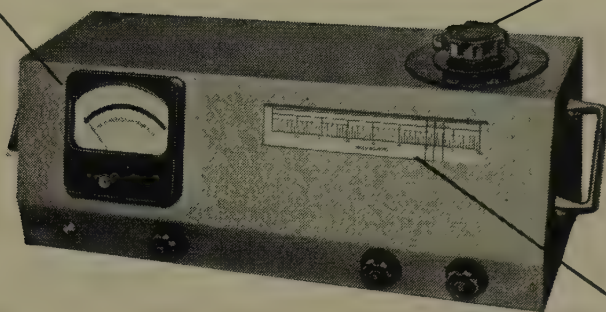
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